Treatability of Wastewaters from High CaO and $CaSO_4$ Content FBC Wastes

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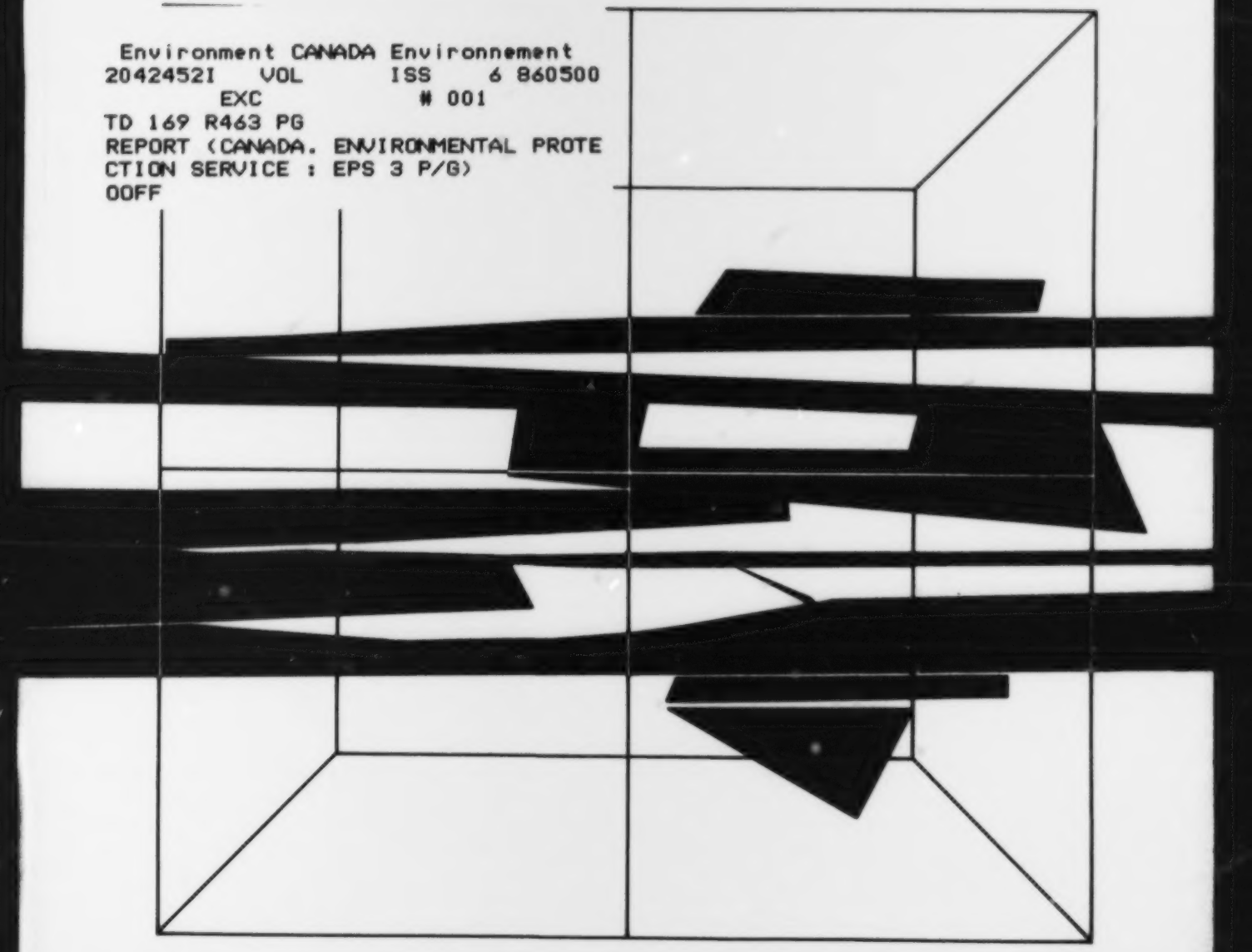

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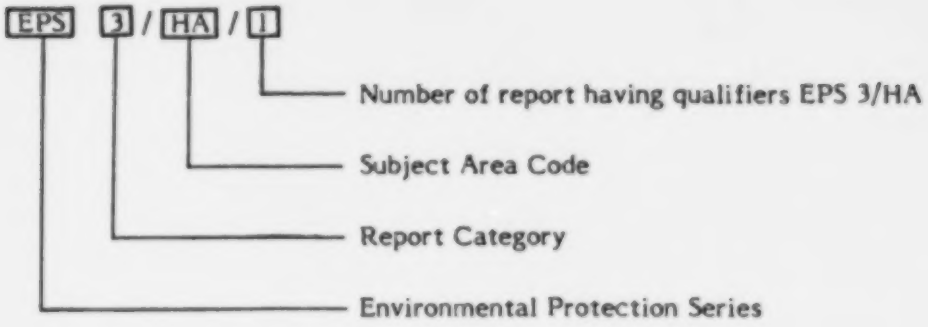

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TREATABILITY OF WASTEWATERS FROM HIGH CaO AND $CaSO_4$ CONTENT FBC WASTES

by

Dearborn Environmental Consulting Services

for the

Industrial Programs Branch
Environment Canada

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ABSTRACT

Atmospheric fluidized bed combustion (AFBC) technology is increasingly recognized as the preferred method of use for the combustion of problem solid fuels such as high sulphur coals. Wastewaters from water contact with relatively soluble AFBC solid wastes may be detrimental to aquatic systems if discharged untreated. This study examines problems anticipated in successful treatment of wastewaters generated from water contact with high calcium oxide (CaO) and calcium sulphate ($CaSO_4$) content combustion wastes.

Literature describing the characteristics of AFBC wastewaters is critically reviewed, focussing on the parameters of major concern such as trace metals, high pH, high alkalinity, and high TDS (total dissolved solids) concentrations consisting mainly of calcium and sulphate ions. The potentially applicable treatment methods of acid addition, recarbonation, aeration, and a combination treatment of recarbonation/aeration are also examined.

Based on the above, a preliminary laboratory - scale treatability study of AFBC wastewaters was conducted. Results are presented and assessed to determine the performance and technical and economic feasibility of various treatment methods. Recarbonation and/or aeration treatments appear to be among the most promising methods. Treatment methods are also assessed according to their stability for small- and large-scale applications and for long- and short-term development.

RÉSUMÉ

La combustion en lit fluidisé (CLF) est de plus en plus reconnue comme la meilleure méthode de combustion des combustibles solides qui, comme les charbons à teneur élevée en soufre, posent des problèmes. Les déchets liquides résultant du contact de l'eau avec les déchets solides relativement solubles de la CLF peuvent être nuisibles pour les systèmes aquatiques s'ils sont rejetés sans avoir été traités. L'étude examine les problèmes prévus résultant du traitement efficace des déchets liquides provenant du contact de l'eau avec des déchets de combustion à teneur élevée en oxyde de calcium (CaO) et en sulfate de calcium ($CaSO_4$).

Les publications décrivant les caractéristiques des déchets liquides de la CLF font l'objet d'un examen critique où l'accent est mis sur les paramètres importants comme les métaux à l'état de traces, les fortes valeurs du pH et de l'alcalimité ainsi que les concentrations élevées de solides totaux dissous (STD) qui comprennent surtout des ions calcium et sulfate. Les méthodes de traitement d'application possible, comme l'addition d'acide, la recarbonatation, l'aération et l'emploi de ces deux dernières techniques à la fois sont aussi étudiées.

Compte tenu de ces possibilités, une étude préliminaire portant sur le traitement des déchets liquides de la CLF a été effectuée en laboratoire. Les résultats sont présentés et évalués en vue de déterminer le rendement des diverses méthodes de traitement ainsi que leur faisabilité du point de vue technique et économique. La recarbonatation et l'aération, ou ces deux techniques à la fois, semblent compter parmi les méthodes les plus prometteuses. Les méthodes sont aussi évaluées en fonction de leur stabilité pour ce qui est des applications à petite et à grande échelles et du développement à court et à long termes.

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1 INTRODUCTION

Atmospheric fluidized bed combustion (AFBC) technology is rapidly gaining acceptance for the combustion of problem solid fuels such as high sulphur coal. In the coal combustion process, coarsely crushed coal, together with limestone, is suspended in the combustion chamber through the injection of fluidizing air from below the bed. During combustion, the limestone is calcined to calcium oxide (CaO), which combines with both the sulphur dioxide (SO_2) released during combustion and oxygen to form calcium sulphate. The control of sulphur emissions is accomplished within the combustion chamber which eliminates the need for add-on flue gas scrubber technology.

One drawback of this sulphur capture process appears to be the large quantities of solid residues produced. These are primarily composed of calcium sulphate ($CaSO_4$) and CaO in bubbling FBC units and are quite different from ashes associated with pulverized coal combustion technology. Preliminary data suggest that AFBC solid wastes are relatively soluble and would produce well buffered, very high pH wastewaters, unlike those from conventional pulverized high sulphur coal combustion wastes. Treatment methods for AFBC wastewaters, therefore, require investigation in order to develop and demonstrate optimum treatment strategies and waste management practices.

Different types of wastewaters could potentially be generated by the disposal of AFBC wastes. Factors that could theoretically influence the wastewater characteristics include: combustor design and operation, method of disposal, waste composition, amount of infiltration, and the duration of time the waste is in contact with the infiltration. To date, however, the characteristics of wastewaters produced through water contact with different samples of this type of waste are relatively similar and appear to be detrimental to aquatic systems if discharged untreated. Consequently, solid waste management and pollution control will likely be major considerations in the development of AFBC for high sulphur coal combustion due to the large quantities and unusual characteristics of the combustion wastes as well as to the wastewater characteristics.

Other promising coal combustion technologies are also being developed for use with high sulphur coals. One of these, for example, is the limestone injection multistage burner (LIMB). The combustion residues from this process may be similar to those from AFBC, as may the wastewaters produced from contact with the residues. Treatment methods developed for AFBC wastewaters, therefore, may also be applicable to

wastewaters from other combustion wastes produced by direct lime or limestone injection combustion technologies.

This study provides a preliminary evaluation of the treatability of AFBC wastewaters of this type through a literature review and laboratory-scale study, using physical/chemical treatment.

1.1 Study Objectives

An overall objective of this study was to examine the nature of the problems anticipated in the successful treatment of wastewaters generated from water contact with high CaO and $CaSO_4$ content combustion wastes. Another objective was to demonstrate and recommend potentially effective, practicable treatments and promising areas for practicable treatment development for this type of wastewater.

The work program was conducted to fulfill the following specific objectives:

1) Briefly review and summarize previous characterization studies on AFBC leachates, and the treatment problems these findings suggest.
2) Briefly review, summarize, and evaluate existing physical/chemical treatment methods which may be applied to well buffered, high pH wastewaters and describe those which may be most applicable or show the most potential for development into practicable wastewater treatments in small- and large-scale Canadian fluidized bed combustion operations.
3) Briefly review and summarize AFBC wastewater characteristics and compare them with those of similar wastewaters from other industrial processes.
4) Demonstrate the treatment characteristics and the treatability of AFBC wastewaters at the laboratory-scale using simple physical/chemical techniques.
5) Assess the results of the treatability demonstration and recommend: a) the treatment methods which appear to be most suitable for immediate small- and large-scale applications; and b) any methods which appear to be most promising for long-term development.

1.2 Study Organization

This study is part of an ongoing Environment Canada program for the development of sound waste handling, disposal, and environmental protection practices for AFBC wastes in Canada. Laboratory leaching tests have been used to generate leachates from AFBC solid wastes. Characterization of these leachates indicate they may be of potential environmental concern and would therefore require some form of treatment.

The leachates evaluated in this study were generated in the laboratory by leaching residues from a pilot-scale Canadian AFBC facility. These residues were compared to residues produced at a 3 MW Canadian AFBC heating facility. Both FBC units were of the bubbling bed design.

A critical review of pertinent literature led to the selection of treatment methods to be evaluated during the treatability study. A variety of water quality objectives and specific industrial effluent guidelines or regulations were examined. From these, experimental criteria were developed to provide targets or goals for "successful" treatment.

The laboratory work began with a preliminary leaching study based on a statistical experimental design. The results of this study were used as a basis for selecting two representative leachate samples for the treatability study. The treatability of these leachates was then evaluated using various physical/chemical treatment methods which were then judged on the basis of a comparison of their respective problems and advantages in meeting these criteria.

Conclusions and recommendations were made based on the literature and the results of the present study.

2 LITERATURE REVIEW

2.1 Studies on AFBC Wastewaters

This section of the report contains a critical review of the literature describing the characteristics of AFBC wastewaters. The review was limited to studies conducted in Canada and the United States.

2.1.1 Canadian Studies on AFBC Wastewaters. Two laboratory-scale studies were conducted to characterize leachates from solid residues produced during the atmospheric fluidized bed combustion of Canadian coal with Canadian limestone.

In the first study the residues investigated were spent bed and baghouse material which were generated during a test burn at a pilot-scale bubbling AFBC unit operated by Foster Wheeler Development Corporation (1). High sulphur eastern Canadian bituminous coal was combusted with eastern Canadian limestone as the sorbent material. The samples were subsequently stored for several years prior to characterization and leaching.

Each residue was subjected to a serial batch leaching procedure of at least 10 cycles (2). Two liquid-to-solid ratios (4:1 ; 20:1) and two leaching media (deionized water; acidic medium) were used. The acidic medium had a pH of 4.5 and was composed of deionized water, glacial acetic acid, and trihydrate sodium acetate. The residues were radially agitated in closed containers for 18 hours, settled, and filtered through 0.45 µm filter paper prior to analysis. The solids were then contacted with fresh medium for the next leaching cycle.

The leachates were highly alkaline with pH values usually greater than 12, and contained high concentrations of dissolved solids primarily composed of calcium and sulphate, typically greater than 1500 mg/L. Low concentrations of metals, usually less than 1 mg/L, were present in the leachates. This was not unexpected due to the alkaline nature of the leachates.

The second study involved the characterization of leachates from solid residues produced at two different Canadian bubbling AFBC installations (3). These were the Queen's University pilot scale unit and the heating unit at Canadian Forces Base, Summerside, P.E.I. Both units utilized Eastern Canadian high sulphur bituminous coal and eastern Canadian limestone.

Residues were subjected to 20 serial batch leaching tests using deionized water as the leaching medium at a 20:1 liquid-to-solid (L/S) ratio for 24 hours. The

mixtures were radially agitated in closed containers. Following the leaching, samples were filtered through 0.45 μm filter paper prior to analysis.

The resulting leachates were highly alkaline with pH values of between 10.3 and 13.4. Total dissolved solids concentrations decreased to between 4400 and 5500 mg/L in the first cycle, to between 120 and 1700 mg/L by the twentieth cycle. Dissolved solids in the leachates were primarily composed of calcium and sulphate. Minor constituents included chlorides, sodium, potassium, fluorides, silicon, aluminum and strontium. These elements were typically present in concentrations which were an order of magnitude less than calcium and sulphate.

2.1.2 U.S. Studies on FBC Wastewaters. This section summarizes the previous work on laboratory and field leaching tests performed on FBC wastes in the U.S.

The leachability of pressurized FBC bed material at the laboratory-scale was reported by Yaverbaum (4). Unfortunately, the protocol followed for the leaching was not described. The leachates were alkaline (pH 10.6 to 12.1) and contained what were considered to be insignificant quantities of heavy metal ions. The equilibrium calcium and sulphate concentrations appeared to be limited by the solubility of calcium sulphate. In comparison, natural gypsum ($CaSO_4 \cdot 2H_2O$) produced leachates containing approximately the same calcium and sulphate concentrations as the bed material leachates. The runoff leachates (not defined) showed a gradual decrease in pH with increased contact with water.

Continuous and intermittent laboratory-scale leaching tests were conducted using AFBC residues from three bubbling facilities: Babcock & Wilcox Unit (bed, fly ash); Battelle Unit (bed, cyclone); and MERC Unit (bed, cyclone 1, cyclone 2 and baghouse) (5). Leaching methods developed by Westinghouse R&D Center were employed which used an automatic shaker and deionized (D.I.) water as the leaching medium. Continuous shake tests using a liquid-to-solid ratio (L/S) of 10:1, and contact time of 400 hours were employed to produce the greatest contaminant release. Intermittent shake tests involved a series of 10 to 15 cycles of a 72-hour test, using a 3:1 L/S ratio. These conditions were used to provide a rate of leaching as a function of time (72 h x no. of cycles) over an extended period, under worst case conditions.

The leachates from the carryover typically had a lower pH as well as lower calcium and total dissolved solids (TDS) concentrations but higher trace element concentrations than the bed leachates. The concentrations of the major contaminants in the carryover leachate and the total volume of leachate passing through decreased faster than

that of the bed leachate. Based on the results, the potential concerns with the leachates from FBC waste disposal sites were expected to be high pH, TDS, calcium, and sulphate concentrations. The trace elements and total organic carbon (TOC) were not expected to be of concern.

In another group of tests, the leaching property was also evaluated as a function of time through the use of a 200-hour continuous shake test using three different leaching media: D.I. water, CO_2-saturated D.I. water (pH 4), and sodium acetate/acetic acid buffer (pH 4.5). There was no significant difference in the leachates produced from the D.I. water and CO_2-saturated D.I. water medium. The pH of the leachate from the highly alkaline residues decreased only slightly, if at all, when the acidic acetate medium was used (pH 11.4 to 12.1). When the D.I. medium was used, a pH range of 11.9 to 12.2 was obtained. The acidic acetate medium yielded leachates with higher conductivities (8.7 to 14.6 mS/cm) than did the D.I. medium leaching (6.47 to 9.24 mS/cm). This may have been partially due to the higher ionic strength and lower pH of the acetate medium.

Tests were also conducted to evaluate the effect of co-disposal of spent bed and carryover residues. A mixture of the bed, cyclone, and baghouse residues (in the proportions of 60:20:20) from the MERC unit, produced a pozzolanic reaction upon leaching. The concentration of TDS in the leachate decreased rapidly as the mixture solidified, then increased when the solidified mixture was broken. Further testing was conducted on cast and cured 5 cm^3 compacts of PFBC residue (80:20 mix of bed and fly ash) fixed by water addition. Whole compacts produced leachates with lower levels of calcium, sulphate, pH, and TDS than crushed compacts. The crushed compacts, in turn, produced leachates with lower contaminant concentrations than the unprocessed mixture. Codisposal of spent bed and carryover residues and/or curing of the residues prior to disposal, therefore, would likely improve leachate quality.

In order to study the effect of leaching protocols on leachate characteristics, AFBC waste from the Pope, Evans & Robbins unit and six other energy process wastes were each evaluated using four different leaching methods (6):

1) EP Method: open system, acetic acid medium (pH adjustment of mixture to 5 ± 0.2 units at various times) L/S ratio of 20:1, 24-h contact time, stainless steel extractor @ 65 rpm.
2) ASTM-A Method: closed system, distilled D.I. water medium, L/S ratio of 4:1 and 48-h contact time, reciprocating shaker apparatus agitated at 1 Hz.

3) ASTM-B Method: same as ASTM-A method, except the leaching medium is an acetic acid-acetate buffer.

4) CAE Method: same as ASTM-A method, except the leaching medium is CO_2 saturated distilled D.I. water (pH of 4.0) and the L/S ratio is 16:1.

The results of this comparison indicated that the highly buffered alkaline AFBC waste neutralized the acidity of the media used in three of the four test procedures, producing a final pH of 11.7 to 12.3. Both ASTM methods produced the highest concentrations of most inorganic species which was a reflection of the large sample quantity and low L/S ratio used. The quantity of inorganic species leached per gram of waste, however, was significantly higher for the EP method, which was presumed to be a reflection of its rigorous agitation method.

The precision of the methods was measured by the relative standard error for replicate extractions. The ASTM-A method had the best reproducibility, followed by the ASTM-B, CAE, and lastly, EP which consistently had the poorest reproducibility. The acetic acid leaching media of the ASTM-B and EP methods also caused some analytical problems. The acetate ion interfered with the determination of fluoride and chloride when using Ion Chromatograph analysis, and also caused rapid deterioration of the graphite tubes in the Atomic Absorption Spectrophotometer used for metals analysis. In view of these results, the researchers recommended the ASTM-A and CAE as the preferred leaching procedures. This study illustrated the impact of the leaching method on leachate characteristics and their subsequent treatability.

In another laboratory study, bed material and fly ash (cyclone and baghouse) were leached separately by five different methods: EP, ASTM-A, ASTM-B and column percolation using D.I. water medium and sodium acetate-acetic acid buffer medium (7). Solid waste runoffs were also simulated in the laboratory, but no description was provided for the method of generating these runoffs.

The leachates from all the extraction methods had a high pH (11.8 to 12.4), and TDS (2460 to 11 940 mg/L) consisting primarily of calcium and sulphate. The heavy metals concentrations were relatively low, with the highest being boron (0.11 to 2.2 mg/L). The runoffs also had a high pH (11.8 to 12.3) and quantities of heavy metals that were lower than those in the leachates from the same solid wastes. Small amounts of volatile and semivolatile organics were detected in the runoffs. The concentrations of organics were detected in the runoffs and were typically higher in the fly ash runoff than in the bed material runoff. The organics present in highest levels in the fly ash runoff

were phenol (3.1 to 7.5 µg/L), trichlorofluoromethane (1.4 to 3.4 µg/L), and 1,1,1-trichloroethane (0.54 to 1.8 µg/L); and in the bed runoff, trichlorofluoromethane (1.1 to 1.9 µg/L).

It was suggested, based on this laboratory study, that runoff from an AFBC solid waste disposal area would require treatment. This would consist of sedimentation to remove suspended solids, and pH adjustment to meet discharge criteria and reduce heavy metals.

A leaching study was conducted using four AFBC fly ashes collected from tests conducted at the Grand Forks Energy Technology Center (8). Solid residues from the fluidized bed combustion of two lignite coals without limestone sorbent added, a lignite, and a sub-bituminous coal with limestone sorbent added were studied. Two leachate extraction procedures were followed: Environmental Protection Agency's EP Method, and column tests. The latter employed short (9 cm) and long (162 cm) columns, a D.I. water medium, and L/S ratios of 3:1 to 9:1 for 5 to 42 pore volumes.

Excellent agreement was obtained for analyses carried out in duplicate extractions, which contrasts with the poor reproducibility observed for the EP method found by other researchers (7). The two leachates of ashes from coal combusted without limestone sorbent had final pH values of 4.5 and 5.7, whereas the leachates of ashes from coals combusted with limestone sorbent had pH values of 7.6 and 8.9.

The leachates from the column testing contained calcium and sodium as the major cationic species and sulphate as the major anionic species. The TDS, sulphate, and sodium were highest in initial aliquots and decreased with increasing pore volume displacements. Calcium, strontium, and barium were in many cases lower in initial aliquots and increased as the sulphate decreased.

The leachate pH decreased only slightly with increasing pore volume displacements. The pH values appeared to be related to coal type and presence of sorbent material. The column leachate pH was typically about two units higher than the pH of the corresponding samples leached by the EP method.

The behaviour of FBC waste when landfilled was studied using one AFBC and one PFBC waste (9). The wastes included a mixture of bed, cyclone, and baghouse residues from the EPRI/Babcock and Wilcox AFBC unit, and another mixture of bed and fly ash from Exxon Miniplant PFBC unit. Several large field lysimeters made up of layers of FBC waste and geological material (chosen to represent typical landfill settings in the eastern U.S.) were exposed to natural precipitation and temperature fluctuations. A partial matrix of combinations of wastes and geological materials was used to assess a

range of conditions. Control columns consisting of the geological materials only were evaluated in the laboratory.

Field leachates collected below 0.31 m of disposal medium and 0.46 m of waste were high in TDS and sulphate (1000 to 10 000 mg/L), calcium and potassium (100 to 1000 mg/L), and chlorides, sodium and silicon (10 to 100 mg/L). The type of geological material used as the upper layer did not have a major impact on the leachate composition. The laboratory column leachates, composed of only geologic materials, generally contained higher concentrations of fluorides, iron, magnesium and manganese and lower concentrations of potassium, lithium, sodium and silicon than the field cell leachates. Although the laboratory columns were leached with the same quantity of D.I. water as the rainfall input experienced by the field cells, comparison of the laboratory and field leachates may not be entirely valid since the laboratory columns were not exposed to temperature fluctuations and other environmental factors that may have affected the field cells.

In contrast, analysis of field leachates that had passed through an additional lower 0.91 m layer of geological material showed that some contaminants were attenuated while others were mobilized. The species that experienced the highest attenuation for most of the field cells were molybdenum, silicon, boron, and calcium for the PFBC cells, and potassium, molybdenum, silicon and strontium, for the AFBC cells. The highest mobilization was evident for magnesium, aluminum, sodium, titanium, vanadium, zinc, and sulphate for the PFBC cells, and aluminum, boron, calcium, iron, magnesium, maganese, nickel, and zinc for the AFBC cells. The cells containing either shale or alluvium were the most effective in attenuation of the contaminants in PFBC and AFBC waste leachates, respectively.

In a related study, AFBC wastes were sampled from the EPRI/-Babcock & Wilcox and Georgetown University pilot plants, and PFBC waste was sampled from the Exxon Miniplant (10). The testing consisted of laboratory batch extraction, laboratory column, and field lysimeter leaching. A serial, six-step laboratory batch extraction procedure was used, with steps 1 to 3 representing leachate generation components, and steps 4 to 6 representing an evaluation of the potential of soil to attenuate leachate. Extractions were conducted using D.I. water at a 10:1 L/S ratio, at 6 rpm, in a rotator designed to ensure maximum contact with minimum particle abrasion. Lab columns containing waste and geological material were set up to parallel the field cells, and leaching was conducted with D.I. water medium. For comparison, field lysimeters

containing layers of FBC waste and disposal media were also installed as described previously (9).

In both AFBC and PFBC leachates, most species other than calcium, sulphate, and hydroxide were typically present at low concentrations. The behaviour of laboratory batch, laboratory column, and field lysimeter leachates differed considerably in pattern of release. The most notable inconsistency was the lower field leachate pH values (neutral to slightly basic) both above and below the attenuation layer, compared to the alkaline laboratory batch and laboratory column leachates. It was suggested that the internal carbon dioxide environment in the field cells must have been different than that of the laboratory columns. The sealed environment and system agitation in the laboratory batch extraction may account for the higher pH values of the leachates produced by this method.

2.1.3 Summary of Canadian and U.S Experience. Based on the technical literature describing the chemical characteristics of AFBC and PFBC waste leachates, it appears that the parameters of major concern are the high pH, alkalinity, and TDS concentrations consisting mainly of calcium and sulphate. Because of the alkaline nature of the leachates, dissolved metals were generally not found to be present in significant concentrations. The concentrations of major species were greater in the bed material leachates, whereas the trace elements and organics concentrations were usually greater in the fly ash leachates.

The total organic carbon (TOC) was determined in leachates from over thirty AFBC and PFBC wastes covering a wide range of FBC process variations. The TOC was consistently less than 10 mg/L for all leachates except the MERC baghouse leachate which was 30 mg/L. Simulated AFBC waste runoffs were found to contain small amounts of volatile and semivolatile organics. The levels of U.S. EPA priority pollutants were typically less than 1 µg/L; however, phenol concentrations ranged up to 7.5 µg/L.

The major chemical characteristics of the leachates were found to be the same for wastes from combustion with limestone and with dolomite. A comparison between leachates of AFBC fly ashes from combustion with and without limestone sorbent indicated that the pH, sulphate, and copper concentrations were greater, and boron, magnesium, manganese, and zinc were lower in the leachate from waste where sorbent was used during combustion.

Comparisons have been made between laboratory and field lysimeter leachates of AFBC and PFBC wastes. The most significant difference between the lab (batch and column) and field leachates was the consistently more neutral pH of the field leachates.

Most researchers investigating FBC waste leaching acknowledged that some form of treatment of the leachate generated from FBC waste disposal sites will likely be necessary prior to its discharge to receiving waters. However, the treatability of this wastewater has not yet been examined and demonstrated in detail.

2.2 Review of Neutralization of Alkaline Wastewaters

As the preceding literature review on FBC wastewaters indicates that these alkaline and highly buffered wastewaters will require treatment, the following is a review of some potentially applicable treatment methods.

2.2.1 General Treatment Methods for Alkaline Wastewaters.

Acid Addition. Adjustment of a high pH can be accomplished by acid addition. Two of the most practical and commonly used reagents for alkaline wastewater neutralization are sulphuric acid (H_2SO_4) and hydrochloric acid (HCl) (11,12). The neutralization reactions for these acids are:

Sulphuric Acid: $(Ca^{+2} + 2OH^- + H_2SO_4 \rightarrow CaSO_4\downarrow + 2H_2O)$ (1)

Hydrochloric Acid: $(Ca^{+2} + 2OH^- + 2HCl \rightarrow Ca^{+2} + 2\,Cl^- + 2H_2O)$ (2)

From the stoichiometric relationships shown in Equations 1 and 2, to neutralize 1 mole of alkalinity as $Ca(OH)_2$ requires 1 mole of H_2SO_4 or 2 moles of HCl. The concentrations of commercial acids are 93.19% for sulphuric acid and 31.45% for hydrochloric acid (12).

As H_2SO_4 is substantially more dense and viscous than water, it does not diffuse well when added to a much larger volume. Techniques to improve dispersion of this acid are discussed by Moore (11). Also, the density and viscosity of the undiluted acids can affect the control and metering of the chemical. Proper system design for acid addition, including feed systems, is discussed in the Water Pollution Control Federation's Manual of Practice No. 8 (12). The hazardous and corrosive nature of concentrated acids demands special handling, maintenance, and safety considerations as well.

Although sulphuric acid is the most widely used acidic reagent, local economic considerations, availability, and the undesirable salts produced when neutralizing with H_2SO_4 may favour the use of HCl.

As there is no direct correlation between alkalinity and pH, the amount of acid required to neutralize a wastewater must be determined by developing laboratory titration curves that show pH versus acid addition per unit volume of sample. Subsequently, reaction rate curves would be prepared to determine the relationship between pH

and time for selected reagent dosages at the mean process temperature and mixing regime. This step would be followed by a bench and/or pilot-scale treatability study.

Recarbonation. Treatment of alkaline wastewaters can be accomplished using the recarbonation process whereby carbon dioxide (CO_2) gas is injected into the wastewater (13). This process has typically been used in lime-soda softening plants as well as for other lime treated wastewaters. The basic purpose of recarbonation is the downward adjustment of the pH of the wastewater. This places the water in calcium carbonate equilibrium and alleviates the problem of scaling which would occur without the reduction in pH (14). Also, the process results in the precipitation of carbonates which are more acceptable than the soluble sulphates or chlorides that would result if acid addition were used. The efficiency of this process is governed by the rate of contact between the gas (CO_2) and the wastewater.

Recarbonation may be carried out as a one- or two-stage process. The neutralization commences as the carbon dioxide reacts with calcium hydroxide to form calcium carbonate (Equation 3), and subsequently with calcium carbonate to form calcium bicarbonate (Equation 4).

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O \quad (3)$$

$$CaCO_3 + CO_2 + H_2O \longrightarrow Ca(HCO_3)_2 \quad (4)$$

In single-stage recarbonation, the pH of the wastewater is reduced to 7 or any desired value in one recarbonation basin. Little calcium is precipitated in this system because the calcium carbonate resolubilizes, forming calcium bicarbonate when the pH is lowered to below 9.3 approximately. At this point the solubility of calcium carbonate which is reflected by the alkalinity is the lowest. The relationship between the alkalinity of the wastewater and the pH during recarbonation is shown in Figure 1.

Two-stage recarbonation employs two basins for CO_2 injection, separated by a settling tank. In the first stage, the pH is reduced to 9.3, resulting in the formation of calcium carbonate precipitate. The rapidly settling floc is removed in the intermediate settling tank. Further treatment is carried out in the second recarbonation basin where additional CO_2 is added to reduce the pH to a desired value (12). The quantities of CO_2 required to stabilize the wastewater are usually evaluated by performing laboratory tests on the wastewater to be treated.

Carbon dioxide is a clear colorless gas that becomes liquid under pressure. An inexpensive source of CO_2 is the boiler furnace stack gas which can contain between 10 to 15 percent CO_2 (14). If this is not available, special CO_2 generators, underwater burners,

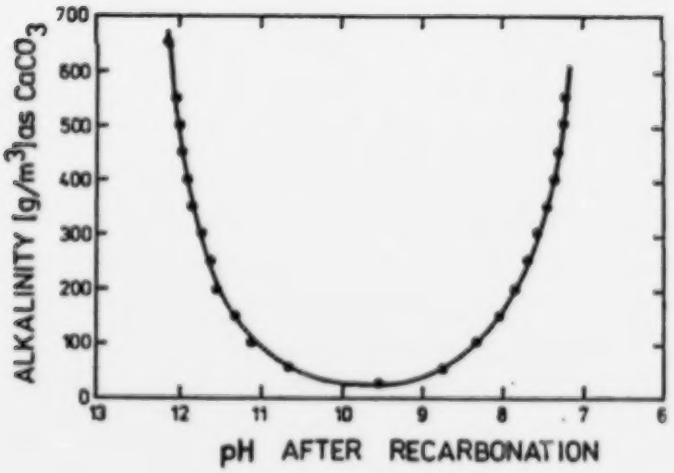


FIGURE 1 RELATIONSHIP BETWEEN ALKALINITY AND pH AFTER RECARBONATION (15)

or liquid CO_2 may be used. Although CO_2 handling does not pose the hazards of acid (H_2SO_4, HCl) handling, there are safety precautions which must be observed (14).

A single-stage recarbonation system requires a residence time of about 5 minutes in the recarbonation basin, followed by about 15 minutes in a subsequent basin to allow the reactions to go to completion. In two-stage recarbonation, a retention time for complete reaction in the two recarbonation basins should be about 15 minutes for cold water and less for warm water. The combination of reaction and settling basin (intermediate settling tank) should have a minimum retention time of 30 minutes.

Carbon dioxide absorption systems often consist of a grid of perforated pipes (typically polyvinylchloride) submerged in the wastewater. The recommended minimum depth of submergence is 2.5 m. Although some researchers (16) refer to the poor solubility of CO_2, others (14) claim that properly designed absorption systems with adequate mixing will transfer 85 to 100 percent of the applied CO_2 to the wastewater. More complete design considerations and information on operation and control of recarbonation are given elsewhere (12,14).

Aeration. This method is less commonly used to treat high alkalinity, high pH wastewaters, although it has been shown to be a viable treatment method (15). Effectively, the process involves solubilizing the CO_2 in the air with the wastewater instead of using pure CO_2 as in recarbonation. The neutralization reactions follow Equations 3 and 4, but the contact time required is substantially longer, as the CO_2

concentration in normal air is about 0.03% by volume. The equilibrium concentration of CO_2 with air is about 0.45 mg/L (14). The solubility of carbon dioxide in water is temperature dependent and decreases with increasing temperature.

The efficiency of the aeration depends on the efficiency of gas transfer. The two-film theory of mass transfer has been used to explain the mechanism of gas transfer. This theory is based on a physical model in which two films exist at the gas-liquid interface. These films, one liquid and the other gas, provide resistance to the passage of gas molecules between the bulk-liquid and the bulk-gaseous phases. For transfer of gas molecules from the gas to the liquid phase, slightly soluble gases such as air and CO_2 encounter the primary resistance to transfer from the liquid film (17). The film gas transfer theory is illustrated in Figure 2.

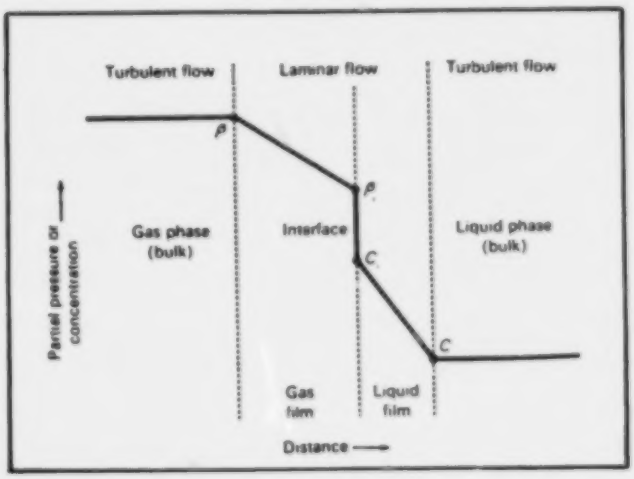


FIGURE 2 SKETCH OF FILM GAS TRANSFER THEORY (17)

The rate of gas transfer is proportional to the difference between the existing concentration and the equilibrium concentration of the gas in solution:

$$\frac{dC}{dt} = K (C_s - C) \qquad (8)$$

where: C = gas concentration

t = time

K = proportionally constant (includes the effect of the resistance of the film(s) and is also a function of the area of liquid-gas interface that exists per unit volume of fluid).

C_s = saturation concentration of gas

The equilibrium concentration of gas dissolved in a liquid is a function of the partial pressure of the gas adjacent to the liquid, as shown in Henry's law:

$$p_g = Hx_g \quad (9)$$

where: p_g = partial pressure of gas (atm)

H = Henry's law constant (@ 1 atm and 20°C, $H_{air} = 6.64 \times 10^4$, $H_{CO_2} = 0.142 \times 10^4$ atm/mole fraction)

x_g = equilibrium mole fraction of dissolved gas

= (moles gas (n_g)/moles gas (n_g) + moles water (n_w))

In wastewater treatment, aeration is commonly accomplished through the dispersion of air bubbles in the liquid at depths up to 4.6 m. Aeration devices include porous plates and tubes, perforated pipes with various configurations of metal and plastic diffusers, and mechanical aerators such as turbine aerators.

For a given amount of air introduced to a liquid system, the available surface through which gas transfer can take place increases to a certain extent with decreasing bubble size. Therefore, improved transfer can be realized with smaller bubbles that have more surface area. Efficient gas transfer also depends on agitation of the wastewater. Turbulence reduces the thickness of the liquid film and lowers resistance to transfer and to dispersion of the dissolved gas once transfer has occurred, therefore, a well mixed system is essential during aeration (or recarbonation) treatment (17).

In practice, mixing of the gas and wastewater is an important concern. The degree of mixing is defined in terms of an energy gradient in the reaction vessel. This parameter is known as the "G" number which has units of s^{-1}. Highly mixed systems have values of 300 or greater.

2.2.2 Treatment of Various Alkaline Wastewaters. No literature was available on the treatment of wastewaters from AFBC residue disposal. The literature was reviewed to find out what treatment methods other researchers have used for various alkaline wastewaters.

A laboratory study was conducted on the treatment of an alkaline wastewater from a lignite coal fly ash pond overflow (15). The treatment methods used were recarbonation and aeration.

Single-stage recarbonation was carried out in a 2-L reactor with reaction times varying from several seconds to 20 minutes. The CO_2 addition was followed by 20 minutes of coagulation/flocculation and 60 minutes of sedimentation. The significant parameter "G" was not specified in this report but based on the description of the test apparatus, it was probably in the range of 200. This indicates that the contents of the reaction vessel were not fully mixed.

The relationship between pH and alkalinity was the same regardless of initial alkalinity (Figure 1). The optimum time of saturation, yielding the maximum degree of calcium carbonate precipitation, was between two and three minutes. Increasing the saturation time to six minutes increased the solubility of the precipitated $CaCO_3$, which became completely solubilized at saturation times greater than six minutes. For an initial alkalinity of 650 mg/L, the maximum calcium carbonate precipitation occurred at pH 9.5, and the residual alkalinity in the effluent remained at 30 mg/L. In comparison, the theoretical solubility of $CaCO_3$ is 15 mg/L @ 18°C. Depending on the initial alkalinity of the wastewater, the CO_2 dosage ranged from 200 to 500 mg/L.

Aeration of the fly ash wastewater was conducted in a 20-L reactor to which air was supplied at a rate of 1 m^3/h. This was followed by one hour of sedimentation. The minimum time of aeration required varied from four to eight hours, depending on the initial alkalinity. The alkalinity reached its lowest value of 30 to 50 mg/L at a pH of 9.5, irrespective of the initial alkalinity. There was no decrease in pH below 7.8. Unlike the one-stage recarbonation, continuing the aeration to pH values lower than 9.5, even up to a contact time of 24 hours, did not increase the solubility of the precipitated $CaCO_3$. This phenomenon may have been due to inadequate mixing resulting in poor transfer efficiency of the CO_2 in the air to the water.

It was suggested that some benefit could be realized by a combination of recarbonation and aeration treatments (15). The extended aeration times required could be shortened by the use of primary recarbonation with pure CO_2 or flue gas until a pH of 9.5 was reached. Aeration would follow to achieve a further decrease in pH.

Literature on various other alkaline wastewaters is primarily from studies conducted in Japan or Russia. Several methods have been used to treat wastewaters from the manufacture of cement and cement-lined cast iron pipe or from construction site

wastewater containing concrete (18 to 24). The treatment methods included recarbonation (19,21,23), or neutralizing the wastewater with $NaHSO_3$, then with $NaHCO_3$ (20).

Dye production wastewaters, with alkalinities of 340 to 850 mg/L as $CaCO_3$, were treated with electrochemical neutralization apparatus using flue gas containing H_2CO_3 (25). Another study described the use of a two-step process treating this type of wastewater with a 90:1 mixture of CaO and $MgCl_2$, and subsequently with 85 percent H_3PO_4 (26). Studies on the treatment of aluminum-containing alkaline wastewaters, reported the use of neutralization with CO_2 gas in the presence of seed materials to precipitate the aluminum (27,28).

Alkaline petroleum wastewaters were treated in one study by mixing them with domestic wastewaters to pH 8.5 to 9.5, followed by aeration for eight to ten minutes at 0.6 m^3 air/m^3 water·min (29). Another alkaline petrochemical wastewater was treated first with an acid or CO_2 to pH 11 and oxidized with an oxygen-containing gas to generate a CO_2 rich gas. This gas was subsequently removed and returned to the first step for pH adjustment (30).

Alkaline wastewater, resulting from the boiler condensate desalination in a boiling water reactor, was recarbonated to a pH of 10.6, filtered, and neutralized to a pH of 8 with H_2SO_4 in an automated operation (31).

2.3 Comparison of Various Alkaline Wastewaters and AFBC Leachates

Detailed information on the characteristics of the various alkaline wastewaters has been published in Japanese or Russian journals but only the abstracts of the papers are available in English. Of the wastewaters studied, fly ash transport wastewater from a lignite fired power plant appeared to be most similar in composition to the AFBC wastewaters, followed by wastewaters from cement manufacture.

The fly ash wastewater was comparable to most AFBC leachates, as it was alkaline in nature with high pH (11.8), TDS (1300 mg/L), calcium (326 mg/L), and sulphate (220 mg/L) concentrations. The concentrations of these parameters were typically somewhat lower in the fly ash wastewaters than in AFBC leachates. Wastewaters from cement manufacture were alkaline in nature, and the major species was likely calcium, due to the lime component of cement. In this respect, cement plant wastewaters would also be comparable to AFBC leachates.

Other alkaline wastewaters such as petroleum plant, dye manufacturing, aluminum-containing, and boiler condensate desalination wastewater differ from the AFBC leachates in composition and concentration of contaminants. For these reasons,

some of the methods used to treat these wastewaters would probably not be practical alternatives for AFBC leachate treatment.

Recarbonation, however, does appear to be a feasible method of treating AFBC leachates from a full-scale facility. It has successfully been applied in a study on the treatment of fly ash transport wastewater, as well as on numerous studies on the treatment of cement/concrete manufacturing wastewaters. Of the various means of recarbonation, flue gas addition may be the most desirable option for AFBC leachates. However, a treatment system of this type has not been developed yet and its practicability would need to be demonstrated.

Aeration may be the next most likely alternative for a full-scale AFBC facility. A greater contact time, and thus, a larger reaction basin would be required for aeration than for recarbonation. A laboratory study on the treatment of alkaline fly ash wastewaters found aeration to be a practical means of reducing the pH and precipitating the alkalinity. A combination of recarbonation or acid addition to lower the pH to 9.3, followed by aeration to further decrease the pH, or some other combination may be the optimum method for treatment of AFBC leachates.

For pilot-scale and small commercial AFBC units, acid addition could be a practical means of leachate treatment due to the smaller volume of leachate generated. Hydrochloric (HCl) and sulphuric acids (H_2SO_4) are the two most commonly used acids for alkali neutralization. It was necessary to evaluate which one of these would be more technically and economically feasible for AFBC leachate treatment.

3 PRELIMINARY LABORATORY STUDY

This section describes the coal combustion residues from which leachates were extracted in the laboratory. The leachate analysis results and the statistical analysis of these preliminary results, used to select representative leachates for subsequent treatability studies, are also presented.

3.1 Origin and Description of Residues

The AFBC solid wastes used to produce the leachates for this study were obtained from the Queen's University AFBC Pilot Plant in Kingston, Ontario. Samples of the bed, cyclone, and baghouse material were collected on January 11, 1984. In addition, solid waste samples from an AFBC heating unit at Canada Forces Base (CFB), Summerside, P.E.I., were collected on November 8, 1984. The latter samples, consisting of bed and baghouse materials, provided a comparison of the characteristics of pilot-scale and larger scale AFBC waste. Both the AFBC units burned similar high sulphur eastern Canadian coals and used Havelock, New Brunswick, limestone for sulphur capture.

The results of the elemental analyses of the AFBC solid residues are presented in Table 1. The analyses shown were quantified primarily with induced coupled argon plasma spectroscopy (ICAP). Chlorides and fluorides were measured by ion chromatography (IC). Arsenic and selenium were analyzed by atomic absorption spectrophotometry (AA).

The main constituent of the residues was calcium, present at 19.6 to 42.5% by weight. Other elements present in significant quantities were silica (3.1 to 6.1%), iron (1.1 to 13.0%), and aluminum (1.4 to 3.9%). The trace and heavy metals increased with decreasing particle size, while calcium showed the reverse trend.

Table 1 also shows a comparison between the residues produced from the Queen's pilot-scale facility and the heating unit at Summerside. The aluminum, potassium, sodium, and zinc concentrations were somewhat lower in the Summerside bed material compared to the Queen's bed material. Similarly the chromium, lead, magnesium, sodium, and zinc were lower in the Summerside baghouse material compared to the Queen's baghouse material. Nevertheless, most of the constituents, including those representing the target criteria parameters, were present at concentrations in the same order of magnitude in equivalent residue types produced at the Queen's and Summerside units.

TABLE 1 CHARACTERIZATION OF AFBC SOLID RESIDUES

Parameter	Queen's Residue			Summerside Residue	
	Bed	Cyclone	Baghouse	Bed	Baghouse
Aluminum	14 100	22 700	38 500	8 150	34 800
Arsenic	24	29	79	-	-
Barium	102	172	391	60	215
Beryllium	< 0.05	0.90	2.69	0.2	2.9
Boron	34.9	63.2	142	18.7	< 8.0
Cadmium	< 1	< 1	< 1	3	24
Calcium	425 000	353 000	196 000	418 000	109 000
Chromium	23	41	56	14.0	1.0
Cobalt	< 5	< 5	< 5	< 5	51
Copper	10.1	36.3	111	14.4	76.6
Iron	10 800	71 900	130 000	9 350	174 000
Lead	25	80	500	< 5	35
Magnesium	4 160	6 280	4 510	3 890	2 640
Manganese	487	637	451	589	504
Molybdenum	< 20	< 20	< 20	< 20	< 20
Nickel	19	34	67	23	51
Phosphate	180	320	1 190	330	1 930
Potassium	3 900	5 400	7 500	1 900	8 100
Selenium	0.19	0.86	7.00	-	-
Silica	31 000	52 500	61 000	26 600	86 300
Silver	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
Sodium	1 000	2 800	5 400	600	1 000
Strontium	304	206	252	279	148
Titanium	545	795	1 760	658	1 240
Vanadium	22.1	46.3	232	26	108
Zinc	325	1 470	3 750	44	163
Zirconium	19	25	35	15	41

Note: All values in mg/kg

3.2 Leaching Protocol: Conditions and Results of Preliminary Leaching Study

A batch leaching procedure was used to generate leachates from the Queen's University bed, cyclone, and baghouse residues (3). Two leaching media were employed for the extraction. Deionized water of neutral pH was used to simulate non-acidic ground and surface waters. An acidic medium of pH 4.5 consisting of acetic acid (0.082 M) plus sodium acetate (0.045 M) was used to simulate acidic ground and surface waters.

The preliminary leaching study included three liquid-to-solid (L/S) ratios, 4:1, 10:1 and 20:1, and three contact times, 2 h, 8 h and 24 h. These were chosen to provide a range of conditions that might occur during the transport and disposal of the three AFBC residues, and to identify representative leaching conditions.

The leaching was conducted under a combination of these conditions for each leaching medium according to the Latin Square experimental design. This permitted a statistical evaluation of the significance of each variable (i.e., impact of residue type, L/S ratio and contact time on leachate quality for both the acidic and the D.I. water leaching media).

The details of the Latin Square experimental design are given in Appendix A. Nine tests were conducted, each under different conditions, for both D.I. and acidic leaching media. The leachate quality was measured in terms of pH, alkalinity, TDS, conductivity, and calcium. The choice of these parameters was based on the findings of the literature review and previously conducted studies of AFBC leachates.

The results of the statistical analysis showed that for the samples leached by the acidic medium, the leachate quality was not significantly affected by residue type, L/S ratio, or contact time. Consequently the residue type chosen for further acidic medium testing was bed material as it constitutes the major portion of AFBC residues. A L/S ratio of 20:1 was selected because it generated the largest quantity of leachate for the treatability work and allowed comparison with previous leaching studies. A contact time of 24 hours was chosen to allow the development of a parallel between the two medias and further comparisons with previous leaching studies.

The results of the analysis of variance for the D.I. medium indicated that the leachate quality was not significantly affected by the L/S ratio. However, the leachate quality was affected by contact time and residue type, with 24 hours, and baghouse material producing the leachate with the greatest concentration of contaminants. Thus, the contact time and residue type selected for further D.I. medium testing were 24 hours and baghouse material, respectively. As previously indicated, the 20:1 L/S ratio was

retained because it generated the largest quantity of leachate for the treatability study and allowed comparison with previous studies.

From this point on, the leachates will be referred to in terms of the AFBC material they were leached from. Leachates generated by the D.I. medium will be designated "baghouse material leachate", and those generated by the acidic medium will be designated "bed material leachates". To summarize, these leachates were produced under the following conditions:

	Baghouse Material Leachate	Bed Material Leachates
Leaching Medium	D.I. water	acidic solution
L/S Ratio	20:1	20:1
Contact Time	24 h	24 h

4 TREATABILITY STUDY

The details of the treatability studies for the AFBC leachates are presented in this section of the report. The performance of the various treatment methods and their technical and economic feasibility are also discussed.

4.1 Discharge Criteria for Treatability Study

Atmospheric fluidized bed combustion (AFBC) is a relatively new technological development. Neither specific industrial discharge criteria for wastewaters from the process nor specific treatment technologies have been developed yet.

For the purposes of this study, stringent criteria were used as a target for the treatability evaluations. These target criteria were developed based on a review of use criteria and recommended water quality objectives such as the maximum acceptable concentration for domestic consumption, objective concentration for domestic consumption, and the guidelines for the protection of freshwater aquatic life as developed by Environment Canada (32). Reference was also made to the discharge criteria for wastewaters from coal fired steam electric generating stations and to previous chemical characterizations of laboratory-produced leachates from AFBC solid residues (33). Selection of the concentrations of criteria parameters was also based on the precision and accuracy of analytical methods available within the limitations of the study.

The criteria used for this study and several other criteria for comparison are shown in Table 2.

4.2 Characteristics of Leachates Used in the Treatability Study

The two leachates selected for the treatability study using the results of the preliminary study were characterized for the parameters shown in Appendix Table C1. These parameters were chosen based on the findings of previous studies on residues from the same AFBC facilities (1,3). The two leaching media were also characterized. The original acidic medium contained high TDS and high conductivity due to its sodium-acetate/acetic acid composition.

The principal constituents of the leachates were calcium (1820 to 3190 mg/L) and sulphate (1300 to 1520 mg/L). The lesser components in both the leachates were, in order of decreasing concentrations: chlorides, sodium, strontium, fluorides, lead, barium, zinc, and boron. The concentrations of the lesser components were at least an order of magnitude lower than the calcium and sulphate. As the arsenic concentration was

TABLE 2 EXPERIMENTAL AND REFERENCE DISCHARGE CRITERIA

Parameter	Experimental Discharge Criteria	Maximum Acceptable for Domestic Consumption (32)	Objective for Domestic Consumption (32)	Guidelines for Protection of Freshwater Aquatic Life (32)	Proposed Discharge Criteria for Steam Electric Generating Stations (32)
pH	6.5 to 8.5	6.5 to 8.5	-	6.5 to 9.0	6.5 to 9.5
Alkalinity	> 20	≥ 30	-	>20	-
Hardness	<120	≤120	<120	-	-
Barium	≤ 0.1	≤ 1.0	≤ 0.1	-	-
Calcium	< 75	≤200	< 75	-	-
Copper	≤ 0.1	≤ 1.0	< 1.0	≤ 0.005	0.5
Iron	≤ 0.3	≤ 0.3	< 0.05	< 0.3	1.0
Nickel	≤ 0.1	-	-	≤ 0.025	0.5
Zinc	≤ 0.1	5.0	< 5.0	≤ 0.03	0.5
TDS	-	<500	-	-	-

Note: All values expressed in mg/L except pH (units).

undetectable at the 0.001 mg/L level and the selenium concentration was very low (0.001 to 0.007 mg/L), these parameters were not included in further characterization work.

The bed material leachate contained more calcium and was comparatively harder and more alkaline than the baghouse material leachate. The baghouse material contained higher concentrations of the trace elements barium, copper, iron and zinc than the bed material. This is in agreement with the work of other researchers who have observed that the major species in AFBC leachates decreased, and the minor species increased, with decreasing particle size (5).

The scaling potential of the raw leachates was evaluated using the Langelier index, which is a function of temperature, TDS, hardness (as $CaCO_3$), alkalinity (as $CaCO_3$) and pH of the wastewater. If the index is negative and dissolved oxygen is present, the wastewater will tend to be corrosive, while a positive index indicates that scale and deposits may form.

Greater scaling potential is associated with larger values of the Langelier Index. The index values for the baghouse and bed material leachates were +7.3 and +7.9, respectively. These values indicate a very high scaling potential. The tendency to form scale would greatly affect the operability of a treatment plant for this type of wastewater, and may reduce the ability to recycle the untreated wastewaters.

The concentrations of the parameters of concern with respect to the discharge criteria are summarized in Table 3. Both raw leachates had very high pH values of 12.4 and 12.5 which exceeded the target pH criteria of 6.5 to 8.5 by at least 4 pH units. The hardness was 4550 mg/L and 7975 mg/L for the baghouse and bed material leachates, respectively. These concentrations exceeded the target criteria of less than 120 mg/L by about 40 and 66 times. Similarly, the target criterion established for calcium of less than 75 mg/L was exceeded 25 times by the baghouse material leachate and 40 times by the bed material leachate.

The concentration of barium in the baghouse material leachate was 0.898 mg/L which exceeded the criterion for that metal of $\leq$0.1 mg/L by nearly an order of magnitude. The barium concentration in the bed material leachate was 0.218 mg/L which was about twice the target value established in this study. The target criterion for zinc of $\leq$0.1 mg/L was exceeded in the baghouse material leachate by a factor of six (0.59 mg/L), while in bed material leachate it just exceeded the criterion at 0.12 mg/L.

The copper, iron and nickel concentrations were below the discharge criteria for both residue leachates. These parameters will not be included in future discussion of

TABLE 3 SUMMARY OF THE UNTREATED LEACHATE CHARACTERISTICS

Parameter	Discharge Criteria	Baghouse Material Leachate	Bed Material Leachate
pH	6.5 to 8.5	12.5*	12.4*
Alkalinity	> 20	2180	5000
Hardness	<120	4550*	7975*
Barium	≤ 0.1	0.898*	0.218*
Calcium	< 75	1820*	3190*
Copper	≤ 0.1	0.017	0.014
Iron	≤ 0.3	0.09	0.09
Nickel	≤ 0.1	0.07	0.09
Zinc	≤ 0.1	0.59*	0.12*

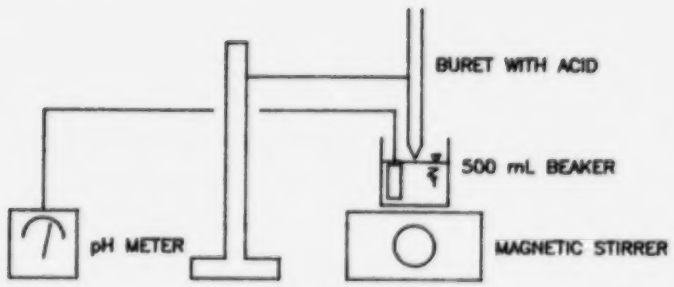
Note: All values expressed in mg/L except pH.
* Concentrations that exceeded the discharge criteria.
Baghouse Material Leachate: D.I. medium, 20:1, 24 h
Bed Material Leachate: Acidic medium, 20:1, 24 h

the discharge criteria in order to focus on the contaminants which exceeded the target criteria. Also, the calculation of hardness based on calcium, magnesium, strontium, iron, aluminum, zinc and manganese revealed that calcium was responsible for greater than 99.9% of the hardness. Therefore, in subsequent discussion, hardness is included as it is reflected by calcium.

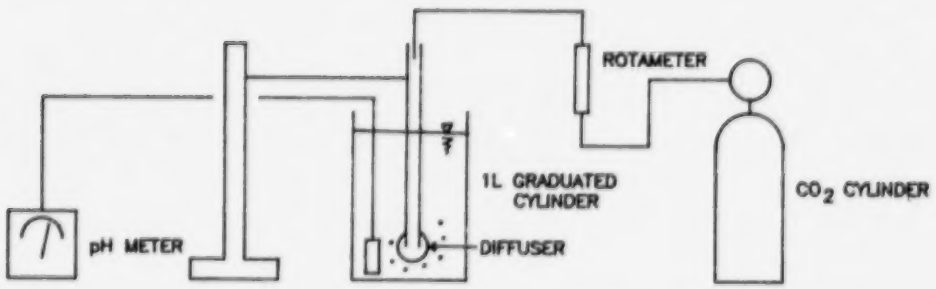
4.3 Results of the Treatability Study

After comparing alkaline wastewaters and treatment methods described in the literature to AFBC leachates, three methods were chosen for this treatability study: acid addition, recarbonation, and aeration. A fourth test, using a combination of recarbonation followed by aeration, was also conducted. In addition, calcium removal was demonstrated using soda ash (Na_2CO_3). Schematics of the laboratory apparatus used for these tests are provided in Figure 3.

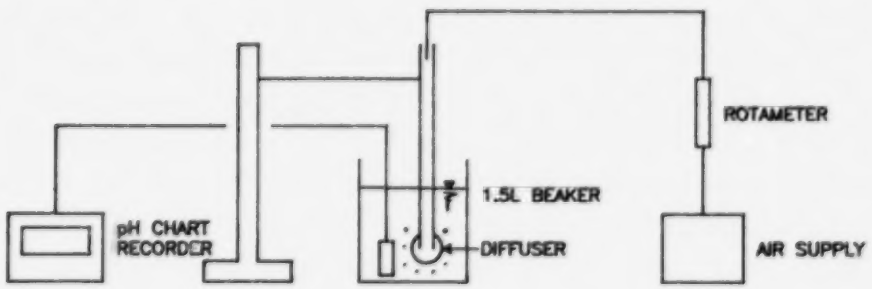
4.3.1 Acid Addition. Following the selection of H_2SO_4 and HCl as candidate reagents for acid addition, titrations were performed with 1.0N acid in an open beaker, to



ACID ADDITION



RECARBONATION



AERATION

FIGURE 3 SCHEMATICS OF LABORATORY APPARATUS FOR TREATABILITY STUDY

determine the quantity of reagent required to neutralize 500 mL of each leachate. The cumulative amount of reagent added and the pH of the sample after each addition were recorded and graphically plotted as shown in Figure 4.

It appears that baghouse and bed leachates treated with either acid expended 95% of the acid demand in lowering the pH from an initial value of 12.5 to 11.0. An additional 3% of the total acid volume lowered the pH further to 10.0, and only 2% was used to decrease the pH from 10.0 to 7.0. It was difficult to control the pH below a value of 10, as depicted by the relatively steep slope between pH 10 and pH 7 (Figure 4). Initially, all the effluents from the acid treatments were clear. After overnight storage in open containers the effluents from the HCl treatment remained free of any precipitate; however, the effluents from the H_2SO_4 treatment contained some precipitate. Analysis of this precipitate revealed that it was primarily calcium sulphate.

The addition of acid may also affect the TDS concentration in the treated wastewater. For example, when HCl was added to the baghouse material leachate, the TDS concentration increased slightly from 5312 to 5622 mg/L. When H_2SO_4 was added to the same leachate, the TDS concentration decreased from 5312 to 2954 mg/L due to the precipitation of $CaSO_4$. This may be viewed as an improvement in the treated effluent quality in terms of TDS; however, it would result in the production of a sludge which must be properly managed.

The neutralization of the baghouse material leachate with HCl and H_2SO_4 produced nearly identical titration curves. This held true for the bed material leachate as well. Titration of the leachates required 45 and 43 mL/L (1.0N acid/sample) for the baghouse and bed material leachates, respectively.

Subsequently, experiments were performed to determine the reaction time of the neutralization reaction using H_2SO_4. The dosage was initially varied between 90 to 110% of the requirements to lower the pH to 7.0 based on previous titrations. The particular amount of reagent was then added all at once to the wastewater, and stirred continuously while the pH was recorded each minute for 10 minutes. The observations of time vs. pH were plotted as reaction rate curves (Figure 5).

The reactions for both leachates occurred in less than a minute. This indicates that a neutralization basin detention time in the order of one minute or less would be acceptable. Examination of the rate curves for the baghouse material leachate reveals that for batch treatment, slightly more than the dosage determined by titration was required to bring the effluent into the desired pH range. The results also illustrate that a

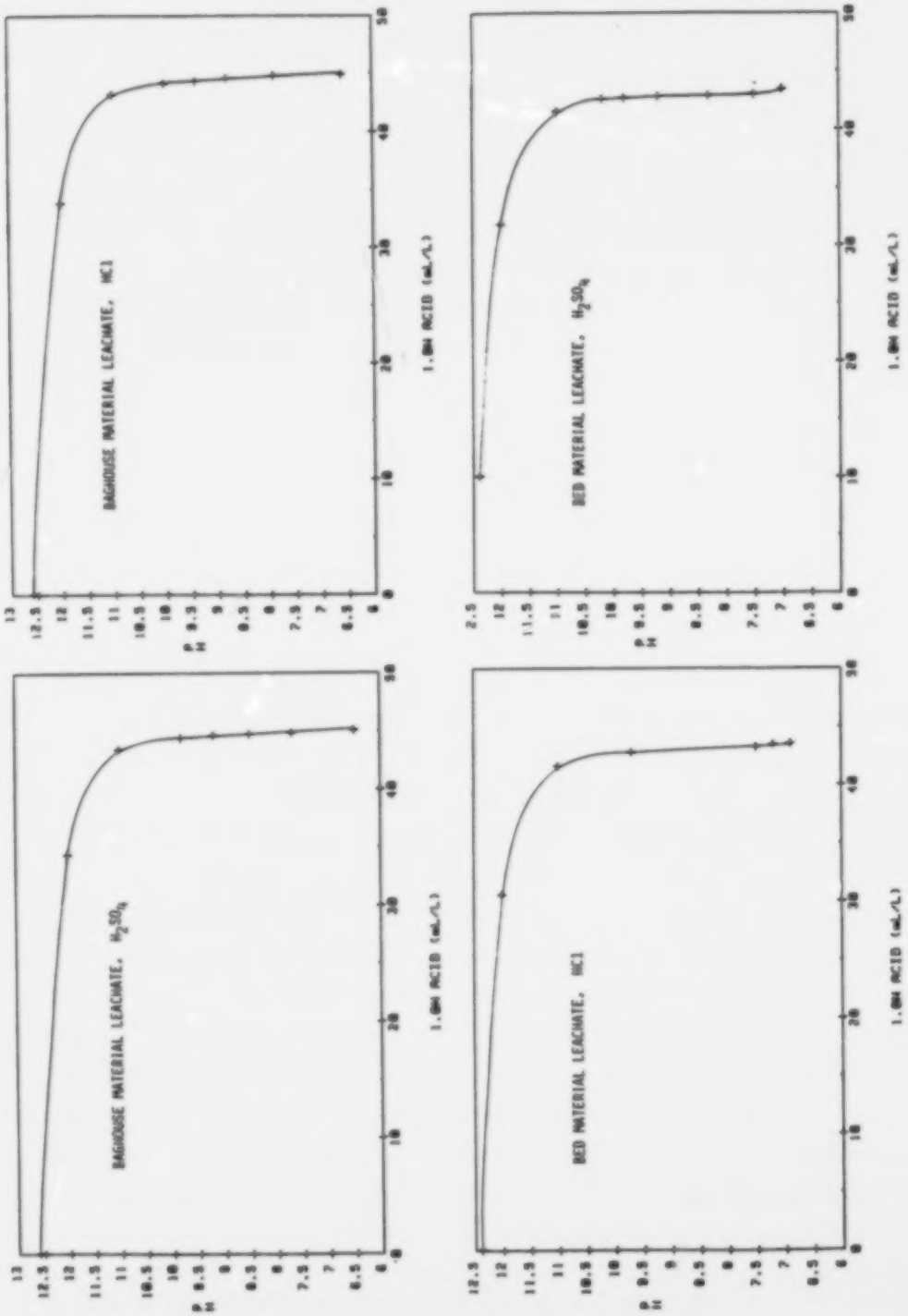


FIGURE 4 TITRATION CURVES FOR TREATMENT WITH ACIDS

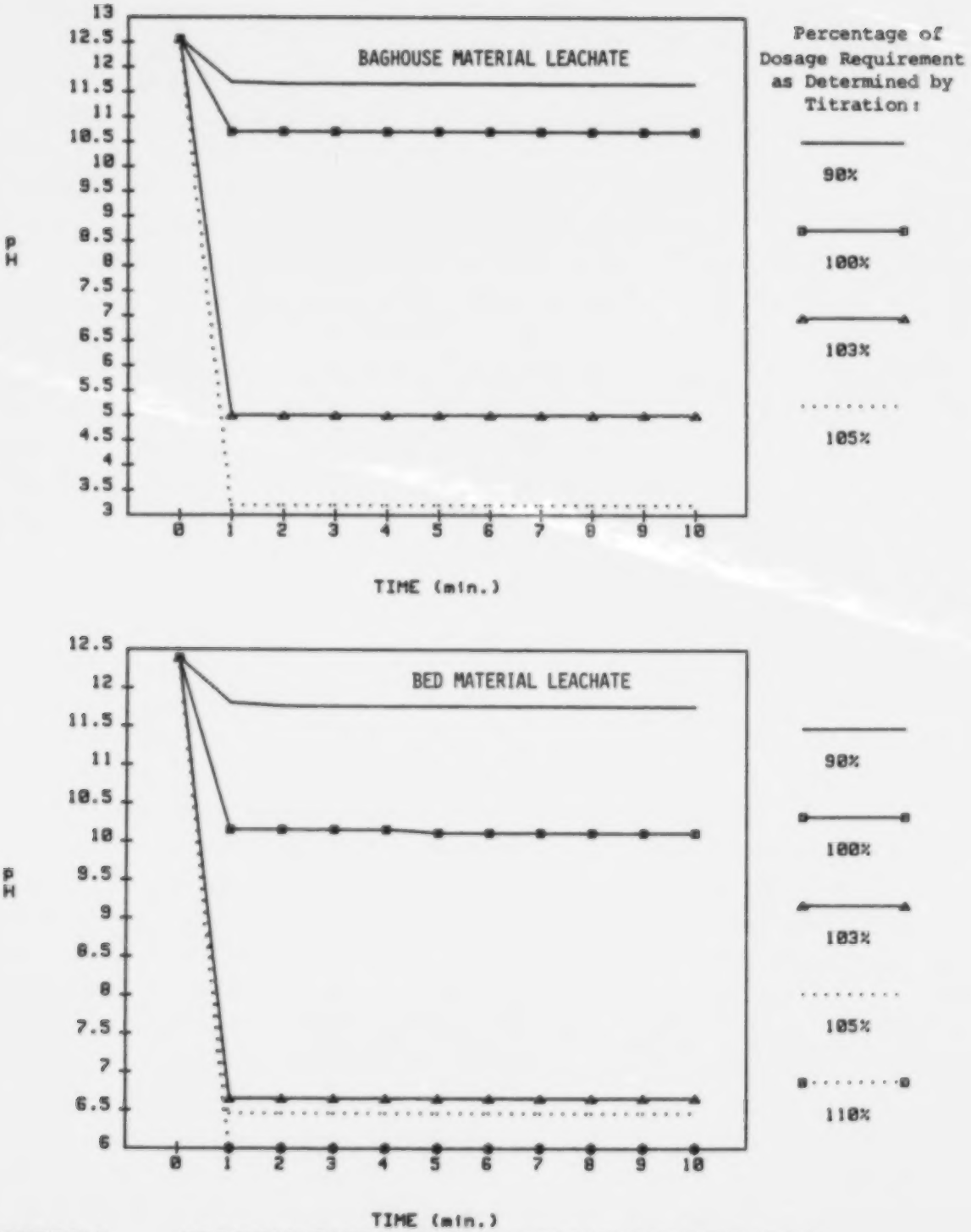


FIGURE 5 REACTION RATE CURVES FOR TREATMENT WITH ACIDS

high degree of pH control would be critical to achieve a target pH of 10 during neutralization with acid since the reaction is hard to control below a pH of 10.

The reaction rate curves for the bed material leachate show similar results. Close pH control would also be advisable for the neutralization of bed material leachate to a target pH value below 10 although it was slightly less sensitive to variation in reagent dose compared to the baghouse material leachate.

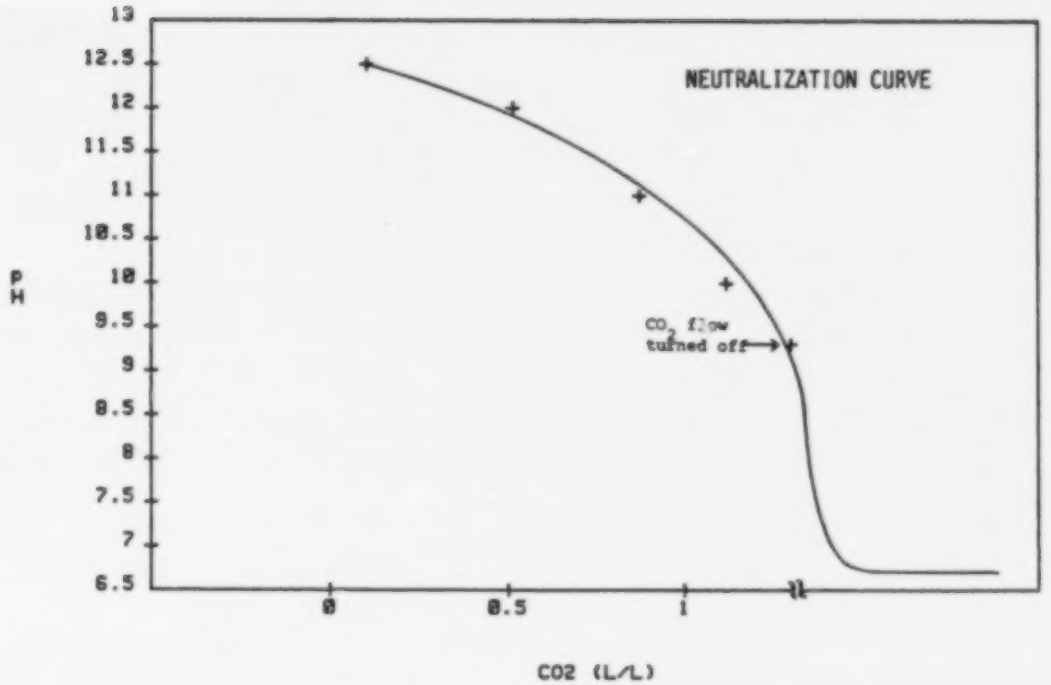
It is estimated from the reaction rate curves for both leachates that 102% of the acid dosage determined by titration should be the optimal dose on which to base the reactor design. Therefore, the sulphuric acid dosages required to reduce the pH to 7.0 would be 46 and 44 mL/L of 1.0N acid for D.I. medium and acidic medium leachates, respectively. Considering the concentrations of commercial grade acids, the following dosages would be required:

	Dosage	
Acid	Baghouse Material Leachate	Bed Material Leachate
H_2SO_4 (93.2%)	1.32 mL/L	1.26 mL/L
HCl (31.5%)	4.60 mL/L	4.40 mL/L

4.3.2 Recarbonation. Treatability tests involving recarbonation were carried out on the leachates using single-stage and two-stage systems. The reactor used for recarbonation had a volume of one litre. The carbon dioxide (commercial grade: 99.5 percent) was supplied by a CO_2 cylinder at a rate of 7.1 L/h and distributed through a diffuser immersed in the sample. The pH was measured and recorded manually.

The velocity gradient (G) during recarbonation was used as a measure of the intensity of turbulence and was found to be 76 s^{-1} during single and two-stage recarbonation. This G value was somewhat lower than the typical G value of 300 s^{-1} used for rapid mixing. The mixing, and therefore, the gas transfer efficiency may have been enhanced by providing mechanical agitation to supplement the agitation created by the gas bubbles. Theoretically, this might have improved control over the reaction.

Single-stage recarbonation, whereby the pH is reduced to the desired value in one step, was carried out on the baghouse material leachate. The neutralization and reaction rate curves show that the reaction occurred within about 12 minutes (Figure 6). The pH was, again, difficult to control below a value of 10. However, a more complex



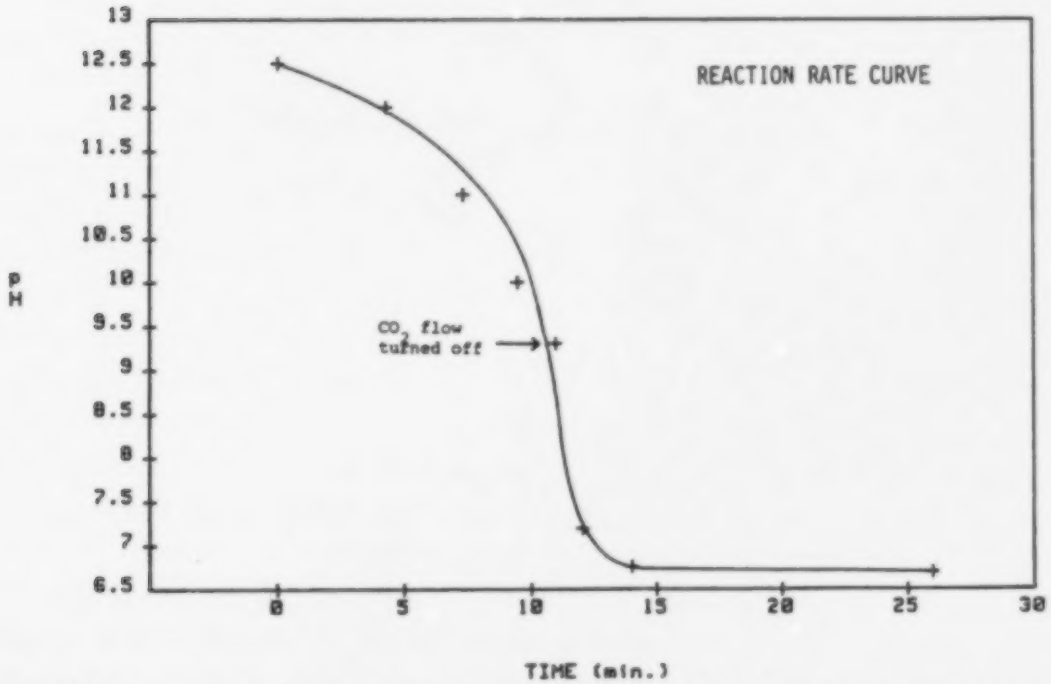


FIGURE 6 SINGLE-STAGE RECARBONATION OF BAGHOUSE MATERIAL LEACHATE

apparatus which incorporated supplementary means to improve gas transfer efficiency may have improved control.

After 11 minutes, and a cumulative CO_2 dosage of 1.30 L/L, the CO_2 flow was turned off when the pH reached 9.3. Subsequently, the reaction continued for an additional 3 minutes, after which the pH levelled off at 6.7.

White fluffy floc was evident upon first contact of the sample with the CO_2. The greatest amount and largest floc appeared between pH 12.5 and 11.0. Additional recarbonation to decrease the pH below 11.0 seemed to break up the floc into smaller particles. After the CO_2 was turned off, the floc floated to the surface while attached to CO_2 bubbles. The floc then settled to the bottom of the reactor, producing a clear supernatant and an estimated sludge volume of less than 1 percent by volume.

Two-stage recarbonation was attempted on both baghouse and bed material leachates. In two-stage recarbonation, the pH is typically reduced to 9.3 in the first stage since calcium carbonate is least soluble at this pH. The results of single-stage recarbonation indicated that it was not possible with this apparatus to stop the reaction at 9.3; therefore, the CO_2 flow was turned off at a pH of 10.3 for the baghouse material leachate and 10.8 for the bed material leachate. The pH continued to decrease and reached a level of 7.8 for the baghouse material leachate, but remained around the same value (11.0) for the bed material leachate, probably due to the greater buffering capacity of this leachate. The inability to control the chemical reaction may have been due to the relatively low mixing regime in the laboratory scale apparatus used. The reaction may have been more controllable if a "G" of 300 or greater had been achieved.

Following the first stage of the two-stage recarbonation, the sample (supernatant and precipitate) was poured into a 1500 mL beaker and slow-mixed for 5 minutes to promote flocculation of the solids. The sample was then subjected to sedimentation for 40 minutes. The supernatant (about 900 mL) was then separated from the sludge, poured back into the original reactor and recarbonated (stage 2) to the desired pH.

Neutralization and reaction rate curves for the two-stage recarbonation of the baghouse material leachate are shown in Figure 7. In the first stage, 0.72 L CO_2/L sample reduced the pH to 10.3 in about 6 minutes. Without additional CO_2 injection, the pH decreased to 7.8. In stage 2, recarbonation required a CO_2 dosage of 0.06 L/L to reduce the pH to 7.1 in about half a minute.

The neutralization and reaction rate curves for the two-stage recarbonation of bed material leachate are also shown in Figure 7. In the first stage, 1.38 L CO_2/L sample

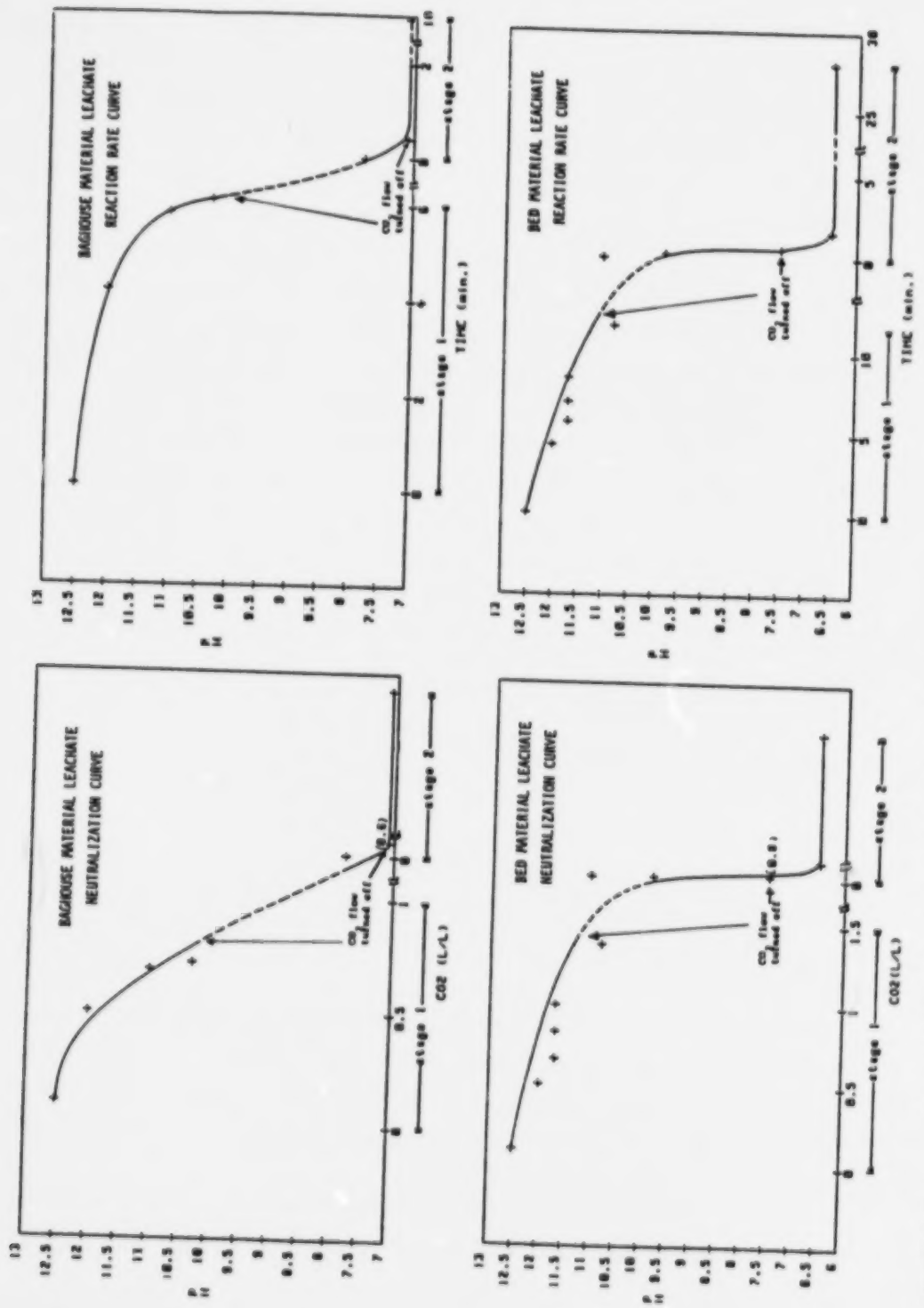


FIGURE 7 TWO-STAGE RECARBONATION OF LEACHATES

reduced the pH to 10.8. After flocculation and sedimentation, stage 2 started at pH 11.0. A CO_2 dosage of 0.08 L/L reduced the pH to 7.5 in about half a minute. The flow of CO_2 was then stopped, but the pH continued to decrease to 6.5 over the next minute and stabilized at that value. Similarly the continued reduction in pH after stopping the CO_2 addition may have been averted by more vigorous mixing in the reactor.

The sludge, resulting from sedimentation of the 1-L recarbonated sample and containing approximately 2 g of dry solids, was poured into an "Imhoff" cone and settled for 30 minutes. It settled rapidly and represented 0.35% by volume for the bed material leachate and 0.30% by volume for the baghouse material leachate. The sludge from the treatment of the bed material leachate was analyzed and found to be composed primarily of $CaCO_3$ (72 percent) and $Ca(OH)_2$ (13 percent).

4.3.3 Aeration. The third leachate treatment method evaluated in the laboratory was aeration. A diffuser connected to the air supply was immersed in 1-L of sample in a 1.5-L beaker. The pH was monitored and recorded continuously on a chart recorder and the air flow was set at the level at which adequate mixing was observed. The air was supplied at a rate of 104 L/h and 85 L/h for the baghouse and bed material leachates, respectively.

The velocity gradient (G) was determined to be 113 s^{-1} and 102 s^{-1} for the baghouse and bed material leachates, respectively. These values were lower than the typical G value of 300 s^{-1} for rapid mix.

Figure 8 shows the relationship between quantity of air required per litre of sample and pH. Ninety-one percent of the total quantity of air used was required to lower the pH from 12.5 or 12.4 to about 10.3. Then, as observed during the acid titration, the slope of the neutralization curve became much steeper and a marginal increase in the dosage of air reduced the pH to 8.0. The pH levelled off at this value for both leachates. Neutralization to a pH of 8.1 required 1560 L of air per litre of sample and 1700 L/L, for the baghouse and bed material leachates, respectively.

The relationship between time of aeration and pH is also presented in Figure 8. The time required to reduce the pH to 8.1 was approximately 15 hours for the baghouse material leachate and 20 hours for the bed material leachate.

During aeration, the samples became turbid, resulting in the deposition of fine crystalline scale on the sides of the beaker. As the amount of solids was relatively small, the quantity of sludge generated was estimated by subtracting the TDS concentration in the effluent from that found in the influent. The sludge loss was 0.19% from the

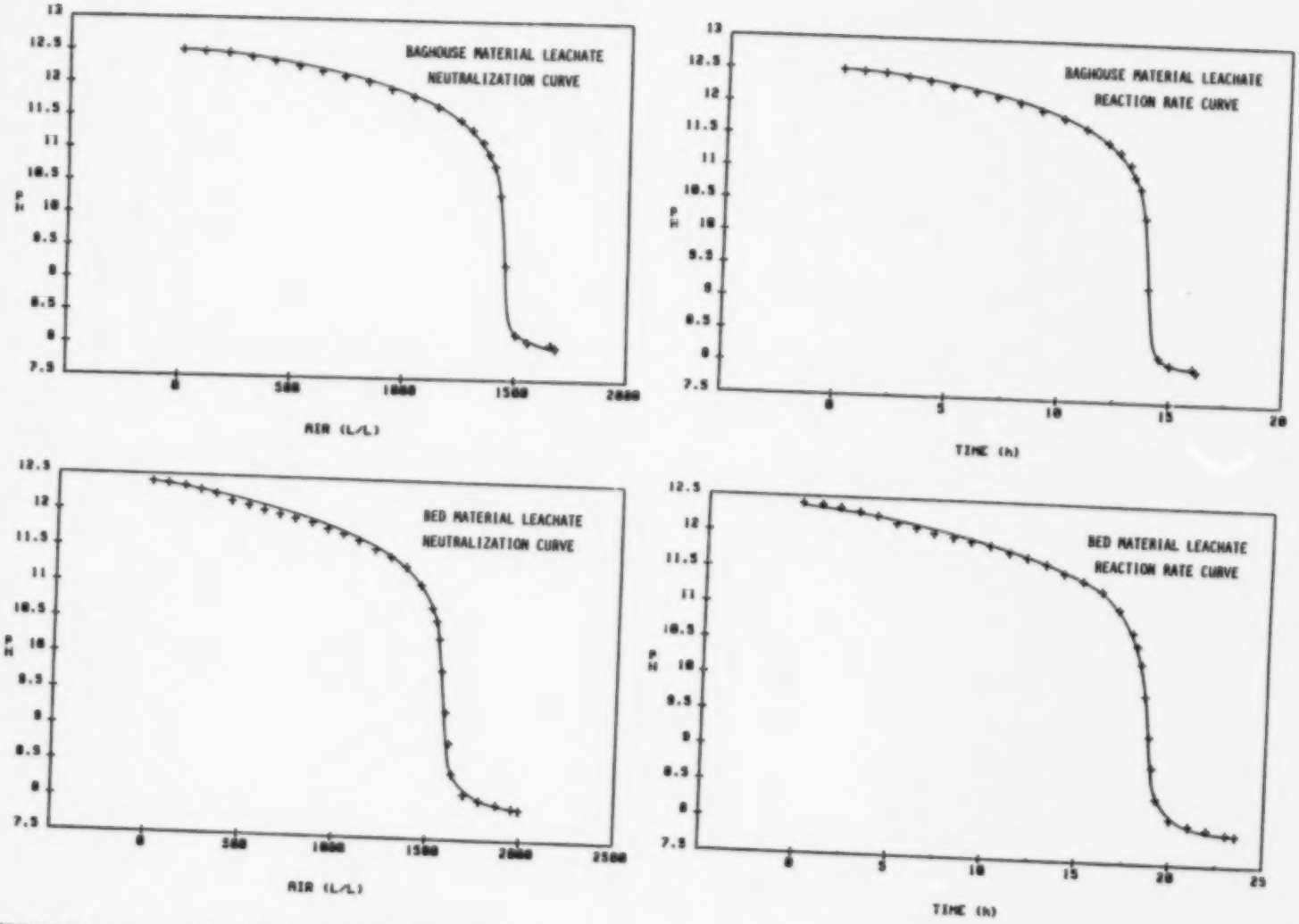


FIGURE 8 AERATION OF LEACHATES

treatment of baghouse material leachate, and 0.12% from the treatment of bed material leachate. The sludge was not analyzed but it was likely composed of calcium carbonate.

4.3.4 Combination Treatment: Recarbonation/Aeration. In order to evaluate the potential advantages of combining two methods, a sequence of aeration and recarbonation was evaluated. The extended reaction time required for aeration was shortened by employing primary recarbonation followed by aeration to further decrease the pH. A 1-L sample of bed material leachate was used for this evaluation.

Recarbonation of the bed material leachate was carried out in a 1-L graduated cylinder at a CO_2 addition rate of 7.08 L/h. The following results were achieved:

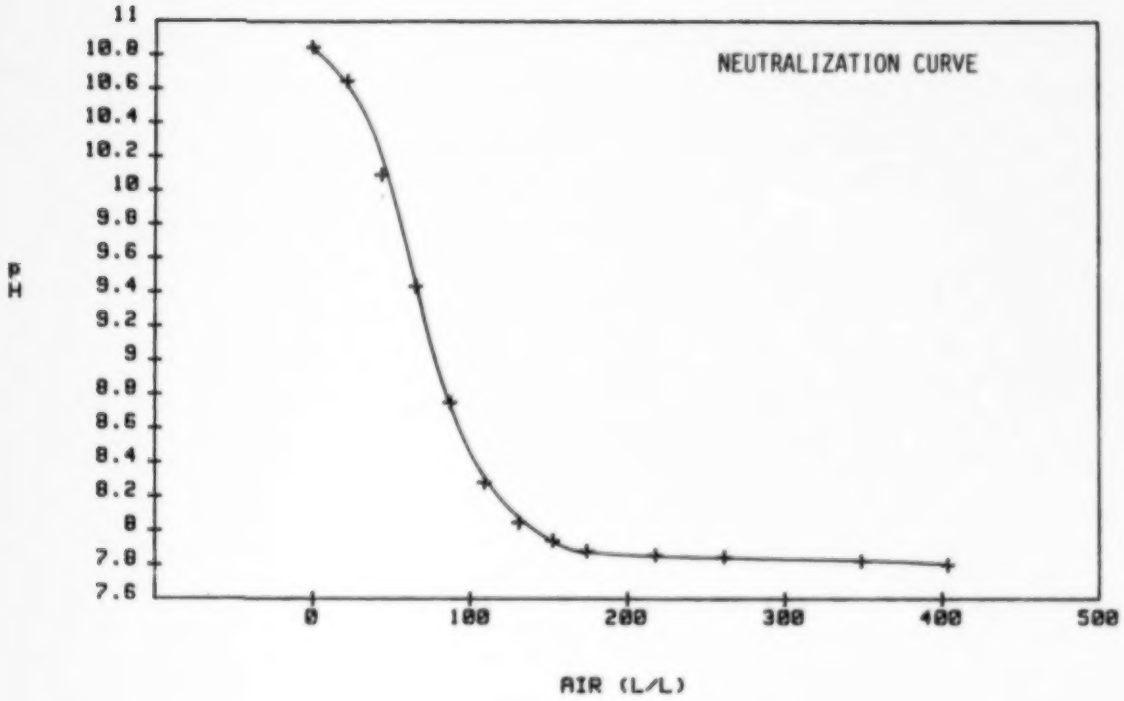
Time (min)	pH	CO_2 (L/L)
0	12.5	0
4.20	12.0	0.5
5.67	10.5	0.7

White fluffy floc was evident throughout the vessel during recarbonation. The CO_2 flow was turned off when the pH reached 10.5 (5.67 min). The sample was then poured into a 1.5-L beaker and mixed at 30 rpm for 5 minutes. After 40 minutes of settling, the supernatant (975 mL) was separated from the sludge which amounted to 0.16 percent by volume.

Subsequently the supernatant (pH 10.9) was aerated in a 1.5-L beaker at a rate of 85 L/h. The neutralization and reaction rate curves for the aeration of the recarbonated sample are shown in Figure 9. This figure shows that the recarbonation step preceding aeration dramatically decreased the aeration time required to achieve a comparable pH reduction. To reduce the pH of the same sample to about 8.0 required 20 hours by aeration alone (Figure 8), but only 1.5 hours using primary recarbonation and then aeration (Figure 9).

The slope of the neutralization curve was relatively steep between the pH values of 10.9 and 8.5. Approximately 140 L of air per litre of sample were required to lower the pH to 8.0. The pH then decreased to about 7.8 after 2 hours (170 L/L). Further aeration did not reduce the pH of the sample below 7.8.

4.3.5 Calcium Removal. The calcium concentration in the baghouse and bed material leachates and treated effluents exceeded the discharge criterion of 75 mg/L. Therefore, preliminary jar tests were performed to evaluate calcium removal. Soda ash (Na_2CO_3) addition was the method selected for this treatment. The procedure involved



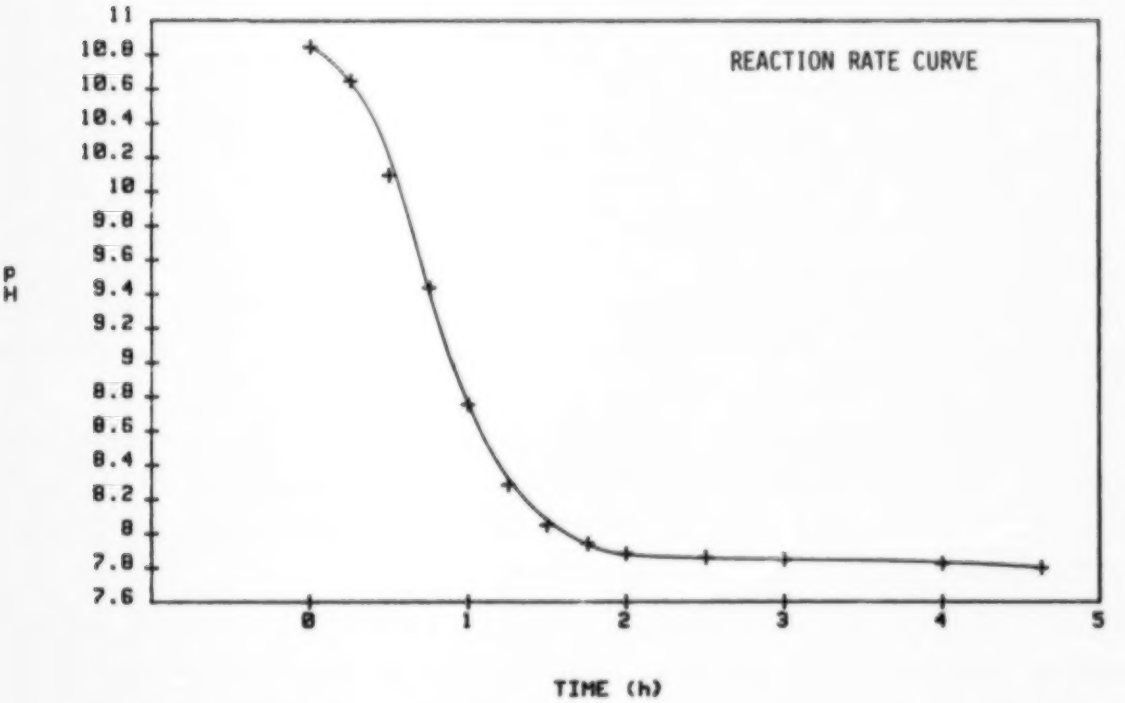


FIGURE 9 **AERATION OF RECARBONATED BED MATERIAL LEACHATE**

adding Na_2CO_3 to 500-mL samples at 100 rpm for one minute (rapid mix - coagulation), 60 rpm for five minutes (slow mix - flocculation), then settling for 30 minutes (quiescent settling - sedimentation).

The calcium removal tests were conducted on the raw and H_2SO_4-treated baghouse material leachates. These samples were chosen arbitrarily to demonstrate the removal of calcium using this technique on an untreated and treated sample. Calcium removal using soda ash was also conducted on a bed material leachate which was different from the bed material leachate used for all other testing. This was done in order to verify the applicability of the treatment to leachates generated under different conditions. The leachate which was derived using acidic medium, a L/S of 10:1 and a contact time of 8 hours, was pretreated with single-stage recarbonation.

The results of the laboratory-scale calcium removal demonstration are shown in Table 4. For the raw baghouse material leachate, 4500 mg/L of soda ash reduced the calcium to 5 mg/L; however, the pH remained at 12.5. The H_2SO_4-treated baghouse material leachate also reached an acceptable calcium concentration (<1 mg/L) at a soda ash dosage of 4500 mg/L, but the pH increased to 10.6. The similarity between the soda ash dosage required for the raw and sulphuric acid-treated leachate appeared to be due to similar calcium concentrations, as there was no precipitation observed immediately after the H_2SO_4 treatment. The recarbonated leachate sample required between 6000 and 10 000 mg/L of soda ash to sufficiently lower the calcium. Theoretically two moles of sodium enter solution for each mole of calcium which is precipitated. This would result in similar TDS concentrations before and after treatment; however, the composition of the TDS would be changed through the substitution of sodium for calcium ions.

A precipitate was immediately evident in all the samples upon addition of the soda ash. The floc settled rapidly after the mixer was turned off. The sludge quantities were estimated to be less than 5% by volume. Based on the following reaction chemistry, this was probably mainly composed of $CaCO_3$:

$$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + Na_2SO_4$$

It is important to note that the soda ash treatment was not optimized, as it was only intended to demonstrate this method. The soda ash dosage would require optimization in order to determine the chemical requirements, since the effluent calcium concentrations of 0.4 to 2 mg/L were significantly less than the discharge criterion (75 mg/L). Because the dosage of soda ash affects the effluent pH, optimization of the dosage would likely result in lower effluent pH values.

TABLE 4 RESULTS OF JAR TESTS FOR CALCIUM REMOVAL

Sample	Soda Ash Dosage (mg/L)	Effluent	
		Calcium (mg/L)	pH (units)
Raw Baghouse Material Leachate	0	1820	12.5
	3000	420	12.5
	4500	<100 (2)+	12.5
	6000	<100	12.6
H_2SO_4-treated Baghouse Material Leachate	0	1630	6.6
	3000	360	6.6
	4500	<100 (0.5)+	10.6
	6000	<100	10.7
Recar onated Bed Material Leachate*	0	2560	6.8
	2000	2080	6.9
	6000	600	7.3
	10000	<100 (0.4)+	10.2

Note: * This sample leached with acidic medium, at L/S of 10:1, for 8 hours.
+ Value determined by more accurate analytical technique.

It must be noted that the desirability of calcium ion replacement in solution by sodium ions and the resulting TDS concentrations in the treated wastewaters would be considerations in evaluating the use of this treatment method in actual practice since sodium may be less desirable than calcium ions.

4.4 Performance of the Various Treatment Methods

The effluent from each of the treatments was analyzed and the results are presented in Table 5 for the baghouse material leachate and Table 6 for the bed material leachate. More complete characterization of the effluents is presented in Appendix C.

Baghouse Material Leachate. The baghouse material leachate, when treated with sulphuric acid, had a pH of 6.5 which met the discharge criterion for pH. It also achieved all the target criteria for metals except for zinc (0.60 mg/L). The alkalinity was reduced to 14 mg/L which is just below the minimum criterion. The calcium was reduced slightly to 1630 mg/L immediately after H_2SO_4 treatment; however, a small amount of

TABLE 5 RESULTS OF TREATABILITY STUDY ON BAGHOUSE MATERIAL LEACHATE

Parameter	Discharge Criteria	Untreated Leachate	Acid Addition		Recarbonation		Aeration	Soda Ash*	H_2SO_4/ Soda Ash
			H_2SO_4	HCl	1-Stage	2-Stage			
pH	6.5 to 8.5	12.5	6.5	6.6	6.6	6.9	7.9	12.5	10.6
Alkalinity	>20	2180	14	22	366	296	44	1970	2960
Calcium	<75	1820	1630	1630	1110	1050	922	2.00	0.46
Barium	≤0.1	0.898	0.031	0.080	0.060	0.143	0.093	0.012	<0.005
Zinc	≤0.1	0.59	0.60	0.56	<0.05	<0.05	0.07	0.10	<0.05

Note: * all values in mg/L except pH (units)
** dosage of 4500 mg/L

TABLE 6 RESULTS OF TREATABILITY STUDY ON BED MATERIAL LEACHATE

Parameter	Discharge Criteria	Untreated Leachate	Acid Addition		Recarbonation (2-Stage)	Aeration	Recarbonation/ Aeration
			H_2SO_4	HCl			
pH	6.5 to 8.5	12.4	7.3	6.9	6.8	7.9	7.7
Alkalinity	>20	5000	2500	2250	2300	2300	2500
Calcium	<75	3190	2010	2900	2320	2250	2190
Barium	≤0.1	0.218	0.172	0.210	0.094	0.112	0.087
Zinc	≤0.1	0.12	0.13	0.13	0.08	0.08	0.08

Note: all values in mg/L except pH (units)

$CaSO_4$ precipitate was produced when the effluent was stored overnight, reducing the calcium to 812 mg/L.

Treatment with hydrochloric acid produced an effluent which was very similar to that produced from the H_2SO_4 treatment, with respect to the discharge criteria parameters. The HCl, however, increased the chloride content of the effluent, as expected. In comparison with the H_2SO_4 treatment, no precipitate was observed in the effluent since chlorides are very soluble.

As shown in Table 5, the single- and two-stage recarbonation produced similar effluents with pH values of 6.6 and 6.9, respectively. The only parameter that significantly exceeded the discharge criteria was calcium at concentrations of 1110 mg/L for single-stage, and 1050 mg/L for two-stage recarbonation. No significant advantage was realized by employing two-stage over single-stage recarbonation, as the majority of the calcium did not precipitate during the intermediate sedimentation step prior to the second stage. This may have been because it was not possible to stop the reaction precisely at 9.3 in stage one. Although the CO_2 flow was turned off at a pH of 10.3, as shown in Figure 7, the pH continued to drop to 7.8 resulting in resolubilization of some of the precipitate formed at a pH of 9.3. Thus a higher target pH of 9.5 may be reasonable in practical terms since the pH adjustment reaction cannot be easily controlled, and a lower target pH could easily be overshot. Also, near pH 9.5, maximum precipitation of calcium carbonate occurs which would reduce the calcium concentration in the treated wastewaters.

Aeration of the baghouse material leachate reduced the pH to 7.9, and alkalinity to 44 mg/L. The barium and zinc concentrations also decreased to less than the discharge criterion of 0.1 mg/L. Again, the calcium concentration of the aerated effluent, 922 mg/L, exceeded the discharge criterion of 75 mg/L.

The soda ash treatment of the raw and H_2SO_4-treated baghouse leachate was effective in reducing the calcium to an acceptable concentration. As discussed earlier, the soda ash treatment was conducted as a demonstration for calcium removal, therefore the dosage was not optimized. Since the calcium concentrations in the effluents of less than or equal to 2.00 mg/L were significantly below the discharge criteria, it may be inferred that the optimal soda ash dosage would be somewhat less than that used (4500 mg/L).

Furthermore, the effluents from the soda ash treatment met the discharge criteria for all the parameters except for pH. The effluent from soda ash treatment of the raw leachate remained at 12.5 while the effluent from soda ash treatment of the

H_2SO_4-treated leachate was 10.6. These results indicate that a more desirable treatment sequence may be to add soda ash first to reduce the calcium and metals, and follow with H_2SO_4 addition to reduce the pH. Again, it can be noted that a judgement of the desirability of this method should include consideration of the exchange of sodium for calcium in the treated effluent.

The Langelier Index of the effluents from the various treatments of the baghouse material leachate is shown in Appendix Tables C2 and C4. The sulphuric acid treated effluent had a Langelier Index of -0.8, indicating a slight tendency to be corrosive. The HCl-treated and recarbonated effluents were neutral, while the aerated effluent (+0.9) had a slight scale-forming potential. The soda ash treated effluents had higher indexes, +4.4 for the leachate treated with soda ash alone, and +2.6 for the leachate pretreated with H_2SO_4, indicating a high and moderate tendency to scale. This was, nonetheless, lower than the scale forming potential of the raw leachate which had a very high positive index of +7.3. Corrosion and scaling potential are of particular interest in recirculating systems.

Bed Material Leachate. Sulphuric or hydrochloric acid lowered the pH of the bed material leachate to 7.3 and 6.9, respectively (Table 6). The raw leachate alkalinity of 5000 mg/L was reduced by approximately one-half by the acid treatment. The acid-treated effluents were, however, not acceptable with respect to calcium, barium and zinc concentrations. The latter two parameters were only slightly above the discharge target of 0.1 mg/L, while calcium concentrations of 2010 mg/L and 2900 mg/L were significantly above the discharge target of 75 mg/L.

The two-stage recarbonation reduced the pH to 6.8, and the alkalinity to 2300 mg/L. The effluent met all the criteria except for calcium. The effluents from aeration and recarbonation/aeration had pH values of 7.9 and 7.7, but in other respects, were very similar to the effluent produced from the two-stage recarbonation. Since the barium concentration of 0.112 mg/L in the aerated effluent was only very slightly above the discharge targets, it was considered to have met the targets satisfactorily.

The soda ash addition for calcium removal was conducted on a sample of bed material leachate generated under a different L/S and contact time than that used for all other bed material leachate testing. The results, presented in Table 7, verified that calcium removal by soda ash addition was effective in the treatment of a somewhat different leachate. The sample was pretreated with single-stage recarbonation which reduced the pH to 6.8 but did not significantly affect the calcium (2560 mg/L). A soda ash dosage of 10 000 mg/L reduced the calcium concentration to 0.41 mg/L and produced

TABLE 7 RESULTS OF CALCIUM REMOVAL DEMONSTRATION ON BED MATERIAL LEACHATE*

Parameter	Discharge Criteria	Untreated Leachate	Recarbonation (Single-stage)	After Recarbonation and Soda Ash**
pH	6.5 to 8.5	12.4	6.8	10.2
Alkalinity	>20	5375	2300	2600
Calcium	<75	2960	2560	0.41
Barium	≤0.1	-	0.105	<0.005
Zinc	≤0.1	-	<0.05	<0.05

Note: all values in mg/L, except pH (units)
* leached at a L/S of 10:1 for 8 hours with acidic medium
** 10 000 mg/L
(-) not determined

an effluent which met all the criteria except for the pH which subsequently increased to 10.2. Again, as the dosage was not optimized, it is likely that a somewhat lower dosage would reduce the calcium sufficiently and result in a relatively lower pH.

Additional information on the characteristics of the bed material leachate and effluents is presented in Appendix Table C3. The TDS of the effluents remained between 11 420 and 14 270 mg/L, compared to the raw leachate TDS of 14 320 mg/L. The soda ash addition (Appendix Table B4) increased the TDS by about seven percent. Sulphate, component of the TDS, did not vary greatly from the raw leachate concentration of 1300 mg/L. Strontium, which remained virtually unaffected by all the other treatments, was reduced significantly by the soda ash treatment.

The Langelier Indexes of all the effluents from treatment of the bed material leachate were positive indicating some scale-forming potential. The recarbonated effluent had an index of +1.8 and the acid-treated effluents had indexes of +2.0 to +2.3, indicating a moderate tendency to scale. The aeration and recarbonation/aeration treatment resulted in effluents with indexes of +2.9 and +2.7, respectively, indicating a relatively higher scale-forming potential.

4.5 Technical and Economic Feasibility of the Various Treatment Options

When comparing the results of the treatability study to the discharge targets or "criteria", it should be recalled that these stringent "criteria" were developed for the

purposes of this study only. They were set at these levels, in part, to permit the development of a performance profile for the treatments. They do not reflect the "practicability" considerations commonly employed for the development of wastewater pollution control requirements which are industry-specific. Naturally occurring levels in surface water may often exceed them; therefore, these criteria should be looked upon as target parameters of an experimental nature for the purposes of this study. For this particular technical and economic feasibility evaluation, the parameters have been categorized in the following manner:

1) pH only;
2) pH and metals only; and
3) pH, metals, and calcium/alkalinity.

The "criteria" metals included barium, copper, iron, nickel and zinc. Discussion about calcium is also applicable to the hardness parameter, as previously discussed. The comparison of various treatment methods evaluated in this study is based on the above order of priority (Table 8). Table 8 pertains to both the baghouse and bed material leachate because the same treatments were effective on the same parameters regardless of the source of leachate contaminants.

TABLE 8 COMPARISON OF EFFECTIVENESS OF TREATMENT METHODS IN TERMS OF THE DISCHARGE CRITERIA

Treatment Method	Category		
	pH	Metals	Calcium/Alkalinity
H_2SO_4	-		
HCl	-		
Recarbonation (1-Stage)	-	-	
Aeration	-	-	
Recarbonation/Aeration	-	-	
Soda Ash/H_2SO_4*	-	-	-
Soda Ash/Recarbonation*	-	-	-

Note: * potential methods

From the results of this study, it could be concluded that two-stage recarbonation may not be practical to implement; however, this is based on the mixing regime in the laboratory reactor. More vigorous mixing may yield results which would make this technique viable at a larger scale. It would be very difficult to stop the first stage reaction at a pH of 9.3 with this process. The soda ash treatment as well as the soda ash treatments following pH adjustments by H_2SO_4 addition or recarbonation have also been rejected because they do not meet the pH criteria and the question of sodium exchange for calcium remains. However, a potential treatment method, involving soda ash addition followed by H_2SO_4 addition or recarbonation has been considered and will be discussed.

If pH were the only parameter of concern, treatment with either H_2SO_4 or HCl acid, would suffice. If pH and metals at the target levels were of concern, then recarbonation, aeration, or a combination of the two could be employed. In the case where calcium/alkalinity are added to the categories of pH and metals, it is expected that soda ash addition could reduce the metals and calcium. Subsequent acid addition, recarbonation, or aeration could then reduce the pH and alkalinity.

Table 9 shows the relative costs of materials for the various treatments based on the baghouse material leachate. It is important to note that the information provided in this table pertains solely to the relative costs of materials. It does not take into account other costs such as capital, construction, labour, and maintenance. If these additional costs were included in the analysis, the relative costs of treatment could differ from those presented.

The dosages required were based on the results of the treatability study. The cost of acids was based on 205-L drums, soda ash on 45-kg bags, and carbon dioxide on a 6230-L cylinder. To arrive at the cost of aeration, the following assumptions were made: fine bubble diffused air aeration requiring a centrifugal compressor, 55 kPa pressure, 90% drive and motor efficiency, power cost of 1 ¢/kWh, resulting in $97.31/yr/brake kW. For a 32 L/min (45 000 L) plant, 1560 L air/L leachate requires 50 m^3 air/min. Based on these assumptions, this rate of air flow would require 63.41 brake kW.

If pH were the only criterion of concern, which may be the case in the short term, then it appears that acid addition would be the best option. The acid costs are lower than any other materials cost except air. However, the aeration basin volume requirement would be five orders of magnitude greater than the reactor required for acid treatment.

Hydrogen chloride ($1.29/$m^3$ treated) is somewhat more expensive than H_2SO_4 ($0.73/$m^3$ treated). It was discovered, however, that the effluent from H_2SO_4 treatment

TABLE 9 COMPARISON OF MATERIALS COSTS FOR VARIOUS TREATMENTS*

Treatment	Dosage (L/m^3) (reagent/ leachate)	Reagent Cost (1985) ($/L)	Treatment Cost (1985) ($/$m^3$)		Discharge Criteria Addressed
H_2SO_4	1.32	0.55	0.73		pH
HCl	4.6	0.28	1.29		
Recarbonation	1300	0.0064	8.32		pH
Aeration	1.5×10^6	2.5×10^{-7}	0.37		and
Recarbonation/	700	0.0064	4.48		metals
Aeration	1.7×10^5	2.5×10^{-7}	0.04	4.52	
Soda Ash/	4.5 (kg)**	0.35/kg	1.58		pH,
H_2SO_4	1.32	0.55	0.73	2.31	metals, and
Soda Ash/	4.5 (kg)**	0.35/kg	1.58		calcium/
Recarbonation	700	0.0064	4.48	6.06	alkalinity

Note: * based on treatment of baghouse material leachate
** not optimized

was not stable and formed a $CaSO_4$ precipitate after about 24 hours. In practical terms, to permit the reaction to go to completion would require a very large sedimentation basin with a retention time of approximately 24 hours following treatment in the neutralization tank. However, the additional precipitation decreased the TDS concentration substantially.

Treatment with hydrochloric acid would require a stirred tank reactor with a retention time of about 30 seconds. Batch neutralization may be feasible for small flows while continuous flow neutralization would be preferable for large flows. The reactor design, energy requirements for the mixing system, and pH control and metering equipment required would have to be determined, based on the size of the facility required.

In the long term, if pH and metals are included in the discharge criteria, recarbonation, aeration, or a combination of the two could achieve the criteria. The materials costs for single-stage recarbonation at $8.32/$m^3$ treated is the most expensive option, based on reagent cost. If, however, it is practical to use the CO_2 content of flue

gas, the recarbonation option may become more economical. The recarbonation basin would require a retention time of about 10 minutes.

If a large land area is available, aeration may be the preferred choice. The energy cost for aeration is only $\$0.37/m^3$ treated, but the 15-hour retention time would require a large aeration basin with a volume two orders of magnitude greater than that required for recarbonation. If the availability of land is limited, and/or the fine crystalline scale resulting from aeration presents a problem, a combination of recarbonation and aeration may be more desirable. In this case, a recarbonation basin with a six minute retention time, followed by an aeration basin with a 1.5-hour retention time would be adequate. Over-acidification of the leachate would not be a problem with this method as the aeration does not easily reduce the pH below about 7.9. This is a significant advantage with respect to wastewater treatment plant operability.

For a more sophisticated large plant operating under criteria that include pH, metals, and calcium/hardness/alkalinity, soda ash treatment followed by sulphuric acid addition appears to be the most economical option in this analysis. The materials costs are estimated to be $\$2.31/m^3$ treated. The soda ash would be added to a mixed tank with a retention time of about six minutes. This tank would be followed by a sedimentation basin with about a 30-minute retention time to settle the calcium and metal precipitates. The treatment would be completed with H_2SO_4 addition to a mixed reactor with a 30-second retention time to reduce the pH.

4.6 Quality Control

In order to insure the reliability of the reported analytical results obtained during this study, a limited quantity control program was developed. It involved analysis of both the solid residue and the leachate chemical.

No standard reference material presently exists for AFBC solid wastes. Therefore, in order to evaluate the solid residue analytical methods, a pulverized coal fly ash standard reference material (NBS 1633A) was analyzed and the results were compared to the certified values for that reference material (Appendix Table D1). Because AFBC residues do not have the same glass-like properties as PCF fly ash, it would be expected that the digestion and analytical methods which give acceptable results for PCF fly ash would also be acceptable for AFBC residues.

The measured values for the certified parameters ranged from 83 to 108% and for the non-certified parameters, the recoveries ranged between 83 and 104%. The

results of this comparison indicate that the analytical results for the solid residues can be reported with confidence.

In order to evaluate the quality of the chemical characterization of the raw and treated leachates, the baghouse material leachate was analyzed in duplicate at the beginning and at the end of the treatability program (Appendix Table C2). A comparison of the two sets of analyses shows very little variation. The data indicate that the analytical methods used for the analysis of the leachate were reproducible and that the chemical characteristics of the leachates did not change as a result of storage during the treatability study.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Based on a critical review of the literature, laboratory-scale physical/chemical treatability studies, and an analysis of the resulting data, the following conclusions can be drawn from the study:

1) At present there are no FBC-specific discharge criteria to protect the environment from wastewaters generated from AFBC combustion wastes. Industrial discharge criteria have been developed for large steam-electric power generation (SEPG) facilities and a variety of water quality objectives exist (33). It appears that FBC wastewaters can be treated to meet SEPG discharge criteria and, where necessary, a variety of other objectives. However, existing discharge criteria are largely based on demonstrated practical methods for particular wastewaters. FBC residues and residue-contaminated wastewaters differ somewhat from other wastewaters and may present somewhat different environmental protection concerns and treatment problems. These differences also need to be considered in the interim until optimum discharge criteria are developed.

2) No technical literature which documents the successful treatment of wastewaters from the AFBC process or its solid wastes was found. There is limited literature on the treatment of other industrial wastewaters with similar characteristics. As this limited literature is primarily in Japanese and Russian, assessment of the technical details and relative merits of the described methods will have to await translation. Some literature was available on the treatment of alkaline wastewaters in general. Acid addition and recarbonation were commonly used methods and were demonstrated in this study. Aeration was also suggested as a possible treatment alternative.

3) The laboratory-produced leachates were similar to those produced in other laboratory studies discussed in the literature. The leachates had high alkalinity, a high pH, and TDS composed primarily of calcium and sulphate, as well as low concentrations of metals. The concentrations of major species were greater in the bed material leachate, whereas the concentrations of trace elements were greater in the carryover leachate. One study reported that field lysimeter leachates were neutral in terms of pH in comparison to alkaline laboratory-produced leachates. Thus it may be inferred that laboratory-produced leachates may represent a worst case in terms of the wastewater characteristics and that, in some field situations, partial or complete natural aeration of wastewaters may occur.

4) The treatability study involved various treatment methods including H_2SO_4 and HCl addition, recarbonation, aeration, and soda ash additions and combinations of these methods. The methods were categorized by the discharge targets they were able to achieve. The acid addition met the pH targets; the aeration and recarbonation met the pH and metals criteria; and the combination of soda ash and H_2SO_4 or recarbonation could meet the pH, metals, and calcium/hardness/alkalinity targets. Most of the methods except HCl addition produced some sludge which was typically less than 5% by volume.

5) Titration curves for acid addition and recarbonation indicate that a significant portion of the reagent dose was expended in lowering the pH from its initial value of about 12.5 to 10.0, and a relatively minor percentage of the total dosage reduced the pH further to 7.0. Because the slope of the curve is very steep between 10.0 and 7.0, the reaction would have to be very closely controlled to prevent overshooting and TDS increase. In the case of recarbonation, this may have been due to the mixing regime in the laboratory scale apparatus. Better control may be possible with a more vigorously mixed wastewater which would promote the recarbonation reaction. Similarly, for aeration, a small percentage of the total air dosage reduced the pH from 10.0 to 7.9. However, additional aeration did not reduce the pH further, thus over-acidification would not be a problem with aeration.

6) The untreated AFBC leachates had an extremely high scaling potential as measured by the Langelier Index. In the laboratory tests conducted, some of the treatment methods reduced the scaling tendency; however, most of the treated effluents retained a slight to moderate tendency to scale. This characteristic may seriously affect the operability of a wastewater treatment plant and limit the recirculation of such wastewaters in a water management strategy.

7) The materials costs of the treatments ranged from \$0.37 to \$8.32/m^3 of wastewater treated for aeration and recarbonation, respectively. This does not include other costs such as capital, construction, labour, and maintenance costs which, when taken into account, could change the overall relative costs of the treatments.

8) In the short term, for small-scale facilities, pH adjustment with acid would be the preferred method. In the long term, for a large-scale facility, some combination of soda ash addition to precipitate the metals and calcium followed by acid addition to reduce the pH and alkalinity would probably be the most feasible option. However the acceptability of changes in major TDS constituents and high TDS concentrations in treated effluents may be of concern with these methods.

Recommendations

Based on a critical review of the literature, laboratory-scale physical/chemical treatability studies, and an analysis of the resulting data, the following recommendations are made:

1) The leaching protocol used to prepare wastewaters for treatability study prevents the complete exchange of CO_2 from the atmosphere to the wastewater. This could result in laboratory-produced leachates with higher contaminant concentrations than would occur in actual field situations. These chemical characterizations, therefore, probably represent "worst case" leachates. It is recommended that these combustion residues be examined using other leaching methods to further understand their leaching properties and the treatability of leachates.

2) The technical literature indicates that a mixture of bed and baghouse materials demonstrated pozzolanic reactions. Such mixtures also demonstrated much lower rates of leaching, and leachates with lower concentrations of contaminants. Solid residues from AFBC may not be segregated by type during disposal. It is

recommended that representative mixtures of waste residues be leached and the resulting wastewaters be evaluated in terms of their treatability.

3) This study demonstrated the treatability of AFBC leachates using various treatment methods. Further study is needed to optimize some of the most promising treatment methods. Optimal treatment strategies may involve some combinations of these methods which should also be identified and demonstrated. In addition, a sensitivity analysis should be performed to assess the effect of variation in concentrations of some of the important leachate constituents on the effectiveness of the treatment methods.

4) Pilot-scale treatability studies on AFBC leachates should be conducted in order to identify potential operating problems and provide data for the design of full-scale facilities. Particular emphasis should be placed on the scaling tendency of these wastewaters and the resulting effect on wastewater treatment plant operation.

5) Methods such as acid or soda ash addition would increase the TDS of the treated effluent. These treatment methods should be examined with respect to their effect on TDS species and concentrations. Future incorporation of TDS in the discharge criteria would greatly limit the treatment options for this type of wastewater. Therefore it is recommended that TDS removal methods be evaluated for these wastewaters in order to determine the feasibility of such technology and to develop treatment costs.

6) An important consideration in the recarbonation reaction is gas/wastewater contact. This is in part controlled by the degree of mixing which is measured by the "G" parameter. Treatability studies described in the technical literature have not considered this aspect of the treatment method. Review of the results from this study suggests that vigorously mixed reactors (G greater than 300) may allow the reaction to be more easily controlled. Improving the control would make this method more practicable as an alternative treatment approach. It is recommended that the effects of mixing on the control of the recarbonation reaction be further investigated.

7) Highly alkaline wastewaters from AFBC residue disposal areas may be useful in acid neutralization. It is recommended that utilization of these wastewaters be studied for the treatment of coal pile runoff or other acidic wastewater, or in agricultural applications to adjust soil pH.

8) The characteristics and treatability of wastewaters from AFBC residues appear to be dependent on relatively few major chemical constituents. As such, this system is ideally suited for evaluation using computer chemistry modelling techniques. Therefore, it is recommended that this approach be used in further study of the treatability of AFBC wastewaters.

REFERENCES

1. Dearborn Environmental Consulting Services, "Preliminary Evaluation of Physical, Chemical and Leaching Properties of AFBC Solid Wastes", DSS File No. 01SE.KE405-2-6446, for the Environmental Protection Service, Environment Canada (March 1983).

2. Dearborn Environmental Consulting Services, "Evaluation of Physical, Chemical and Leaching Properties of AFBC Solid Wastes", DSS File No. 01SE.KE405-3-6594, for the Environmental Protection Service, Environment Canada (March, 1984).

3. Constable, T. and P. Côté, "A Proposed Procedure for the Development of a Canadian Data Base on Waste Leachability", Wastewater Technology Centre, Environment Canada, Burlington, Ontario (May, 1981).

4. Yaverbaum, L., "Spent Stone Disposal", in Fluidized Bed Combustion of Coal and Waste Materials, Noyes Data Corp. (1977).

5. Sun, C.C., C.H. Peterson, and D.L. Keairns, "Experimental Engineering Support for EPA's FBC Program: Final Report, Solid Residue Study", U.S. National Technical Information Service, Report PB80-219256 (January, 1980).

6. Bause, D.E. and K.F. McGregor, "Comparison of Four Leachate - Generation Procedures for Solid Waste Characterization in Environmental Assessment Programs", U.S. Environmental Protection Agency, Report No. EPA-600/7-80-118 (May, 1980).

7. Chu, T.Y., D.B. Cox, J.W. Shiee, and L.H. Woosley, "Water Quality and Solid Waste Management for a Proposed TVA Atmospheric Fluidized Bed Combustion Demonstration Plant", Environmental and Economical Considerations in Energy Utilization, 176-188 (1981).

8. Thompson, C.M., "Chemical and Physical Characteristics of Western Low-Rank Coal Waste Materials. Part 2: Byproducts from an Atmospheric Fluidized Bed Combustion System. Final Report", U.S. National Technical Information Service No. DOE/FC/10200-T3 (November, 1982).

9. Grimshaw, T.W., W.M. Little, R.A. Minear, and J.O. Milliken, "Generation and Attenuation of Leachate from PFBC and AFBC Solid Residues in Simulated Landfill Conditions", Proc. Int. Conf. Fluidized Bed Combustion, 7(1), 534-43 (1983).

10. Minear, R.A., T.W. Grimshaw, and A.G. Eklund, "Stepwise Batch Generation of Leachate from PFBC and AFBC Solid Residues: Characterization and Comparison with Field and Lab Column Leachates", Proc. Int. Conf. Fluidized Bed Combustion 7(1), 544-58 (1983).

11. Moore, R.L., Neutralization of Wastewater by pH Control, Instrument Society of America (1978).

12. WPCF/ASCE, Wastewater Treatment Plant Design, Manual of Practice No. 8, Water Pollution Control Federation, Washington, D.C. (1977).

13. WPCF, Operation of Wastewater Treatment Plants, Manual of Practice No. 11, Water Pollution Control Federation, Washington, D.C. (1976).

14. Culp, R.L. and G.L. Culp, Advanced Wastewater Treatment, Van Nostrand Reinhold Company (1971).

15. Dziubek, A.M. and A.L. Kowal, "Treatment of Alkaline Wastewater from Lignite-Fired Power Plants", Water Science Technology, 15: 155-162 (1983).

16. Kurz, G. and V. Trenkle, "Neutralization of Wastewater", Chemical Processing, London, 20 (2): 9-11 (February, 1974).

17. Metcalf & Eddy Inc., Wastewater Engineering, McGraw Hill Book Co. (1972).

18. Sumitomo Cement Co. Ltd., "Treatment of Alkaline Wastewaters", Patent, Japan Kokai Tokkyo Koho, JP8227192, A2, (CA:96(26)222729r) (1982).

19. Takenaka Komuten Co. Ltd., "Neutralization of Alkaline Wastewaters", Patent, Japan Kokai Tokkyo Koho, JP8265385 A2, (CA:97(14)114825f) (1982).

20. Chichibu Cement Co. Ltd., "Neutralization of Alkaline Wastewaters", Patent, Japan Kokai Tokkyo Koho, JP8144090 (CA:95(10)85845p) (1981).

21. Iwatani and Co. Ltd., "Neutralization of Alkaline Wastewater with Liquid Carbon Dioxide", Patent, Japan Kokai Tokkyo Koho, JP83101788 A2, (CA:99(22)181050d) (1983).

22. Takenaka Komulen Co. Ltd., "Neutralization of Alkaline Wastewater", Patent, Japan Kokai Tokkyo Koho, JP8265384 A2 (CA:97(14)114826g) (1982).

23. Azabu Cement Co. Ltd., "Neutralization of Alkaline Wastewater", Patent, Japan Kokai Tokkyo Koho, JP8023116 (CA:94(8)52396u) (1980).

24. Nippon Chutetsu Kan, K.K., "Alkaline Wastewater Treatment", Patent, Japan Kokai Tokkyo Koho, JP82171486 A2 (CA:98(14)113163x) (1982).

25. Gerasimov, A.F. and L.A. Alferova, "Neutralization of Alkaline Wastewaters", Tekst. Prom-st., No. 12, Moscow (CA:96(12)91081y) (1981).

26. Effenberger, M., E. Mattiello, and J. Kinkor, "Treatment of Alkaline Wastewater Containing Carbonates and Organic Compounds", Patent, Czechoslovakia, CS 184573 (CA:95(2)12307e) (1980).

27. Arakawa, N. and M. Murano, "Treatment of Aluminum - Containing Alkaline Wastewater by Seeding and Carbonation", Kogyo Yosui, No. 292, Japan (CA:98(18)149090k) (1983).

28. Arakawa, N. and M. Murano, "Carbonization Treatment of Alkaline Wastewater Containing Aluminum", Kenkyu Hokoku - Kangawa - Ken Kogyo Shikensho, No. 53, (CA:99(14)110149g) (1983).

29. Lutsenko, G.N., A.I. Tsvetkova, N. Tugusheva, A.D. Vinnichenko, L.I. Gyunter, and A.Y. Lerner, "Alkaline Wastewater Purification, Patent, USSR, SU887476A1 (CA:96(20)168148k) (1981).

30. Sterling Drug Inc., "Continuous Oxidation of Alkaline Wastewater", Patent, Japan Kokai Tokkyo Koho, JP82132589A2 (CA:98(6)40110r) (1982).

31. Tokyo Electric Power Co. Inc., and Japan Organo Co. Ltd., "Automatic Neutralization of Alkaline Wastewater", Patent, Japan Kokai Tokkyo Koho, JP8343285A2 (CA:99(10)76275h) (1983).

32. McNealy, R.M., V.P. Neimanis, and L. Dwyer, Water Quality Sourcebook, A Guide to Water Quality Parameters, Inland Waters Directorate, Water Quality Branch, Environment Canada, Ottawa, Canada (1979).

33. Anon., "Environmental Codes of Practice for Steam Electric Power Generation, Design Phase", Environmental Protection Service, Environment Canada, Ottawa, Canada (March, 1985).

APPENDIX A

LATIN SQUARE EXPERIMENTAL DESIGN

APPENDIX A LATIN SQUARE EXPERIMENTAL DESIGN

A 3 x 3 Latin Square was set up in the following manner. One variable (residue type) was assigned as rows, the second (L/S ratios) as columns, and the third (contact times) as treatments. Each box of the matrix represents one experimental unit to which is assigned one of the three treatments. Different permutations are possible; however, each row and each column can contain each treatment only once. The Latin Square design is shown in Table A1.

TABLE A1 LATIN SQUARE DESIGN

	I	II	III
1	A	B	C
2	B	C	A
3	C	A	B

	4:1	10:1	20:1
Bed	2 h	8 h	24 h
Cyclone	8 h	24 h	2 h
Baghouse	24 h	2 h	8 h

The nine tests shown in Table A1 were conducted for both leaching media. The leachate quality was measured in terms of six parameters: pH, alkalinity, TDS, conductivity, calcium, and sulphate. These parameters were chosen as the literature suggested they could be used to characterize AFBC leachates.

Results of Preliminary Lab Study/Latin Square Experiment

The characteristics of leachates from the three residues leached under arious conditions in the preliminary study are presented in Table A2. The results of the preliminary testing were statistically evaluated using the Latin Square design. An example using the Latin Square design is shown in Table A3.

TABLE A2 LATIN SQUARE WITH RESULTS OF LEACHING TEST

	4:1	10:1	20:1	Totals
Bed	(2 h) 3080	(8 h) 2960	(24 h) 3000	9040
Cyclone	(8 h) 3000	(24 h) 2960	(2 h) 2960	8920
Baghouse	(24 h) 3960	(2 h) 3240	(8 h) 3080	10280
Totals	10040	9160	9040	28240
Treatment Totals	2 h 9280	8 h 9040	24 h 9920	Total 28240

The method of calculating the variance is shown below, while the analysis of variance is presented in Table A4.

Total variation: $V = (3080)^2 + (2960)^2 + \ldots\ldots (3080)^2 - (28240)^2/9$

$V = 825956$

Variation between rows: $V_r = (9040)^2/3 + (8920)^2/3 + (10280)^2/3 - (28240)^2/9$

$V_r = 377956$

Variation between columns: $V_C = (10040)^2/3 + (9160)^2/3 + (9040)^2/3 - (28240)^2/9$

$V_C = 198756$

Variation between treatments: $V_t = (9280)^2/3 + (9040)^2/3 + (9920)^2/3 - (28240)^2/9$

$V_t = 137956$

Variation in residuals: $V_E = V - (V_r + V_C + V_t)$

$= 825956 - (377956 + 198756 + 137956)$

$V_E = 111288$

Upon examination of Table A4, the 'f' values for rows (3.40), columns (1.79), and treatments (1.24), were all less than $F_{0.95,2,2} = 19.0$. Thus, it can be concluded with 95% confidence that the acidic medium leachate quality, as measured by calcium, is not significantly affected by residue type, L/S ratio, or contact time. This conclusion held true for every one of the nine acidic medium tests for all six parameters representing leaching quality (Table A5).

TABLE A3 CHARACTERISTICS OF LEACHATES FROM PRELIMINARY LABORATORY LEACHING

Parameter	Leaching Medium	Bed 4:1 (2h)	Bed 10:1 (8h)	Bed 20:1 (24h)	Cyclone 4:1 (8h)	Cyclone 10:1 (24h)	Cyclone 20:1 (2h)	Baghouse 4:1 (24h)	Baghouse 10:1 (2h)	Baghouse 20:1 (8h)	Blank
pH	D.I.	12.5	12.5	12.4	12.5	12.4	12.5	12.3	12.5	12.5	7.4
	Acidic	12.4	12.4	12.3	12.4	12.3	12.5	12.3	12.5	12.5	4.4
Alkalinity	D.I.	2000	2050	2050	2025	2075	2175	2050	2425	2425	< 1
	Acidic	5300	5375	5550	5250	5300	5450	5700	5350	5900	0
TDS	D.I.	4468	4430	4492	5212	4918	4592	8980	6460	5650	< 2
	Acidic	13 728	13 682	14 688	14 944	14 560	14 756	17 988	15 968	14 534	3728
Conductivity	D.I.	8650	8450	9550	10 260	10 200	9040	15 000	11 570	11 980	0.98
	Acidic	13 600	14 000	15 900	14 200	15 400	14 900	21 400	17 400	17 500	3190
Calcium	D.I.	1400	1440	1400	1560	1480	1560	2360	2000	1800	<0.01
	Acidic	3080	2960	3000	3000	2960	2960	3960	3240	3080	0.15
Sulphate	D.I.	1340	1520	1610	1540	1630	1540	1450	1370	1470	< 0.1
	Acidic	1390	1490	1630	1540	1610	1540	1470	1070	927	< 1.0

Note: all parameters expressed in mg/L, except pH (units), and conductivity (µS/cm)

TABLE A4 ANALYSIS OF VARIANCE

	Variance	Degree of Freedom	Mean Square	f	$F_{0.95,2,2}$
Rows (Residues)	377956	2	188978	3.40	
Columns (L/S Ratios)	198756	2	99378	1.79	19.0
Treatments (Contact times)	137956	2	68978	1.24	
Residuals	111288	2	55644		
TOTAL	825956				

Note:
- Degrees of freedom = (m - 1) for an m x m Latin Square
- Degrees of freedom for Residuals = (m - 1) (m - 2)
- Mean square = (variance)/(degrees of freedom).
- f = (mean square)/(mean square of Residuals)

TABLE A5 RESULTS OF ANALYSIS OF VARIANCE

	f Values					
	Residue		L/S Ratio		Contact Time	
Parameter	D.I.	Acidic	D.I.	Acidic	D.I.	Acidic
pH	0	-	0	-	3.0	-
Alkalinity	10.48	5.67	5.59	4.67	2.93	1.33
TDS	7.54	2.92	1.83	0.63	2.66	1.21
Conductivity	52.71	12.04	5.67	0.32	0.96	3.75
Calcium	8.92	3.40	0.71	1.79	0.42	1.24
Sulphate	23.38	5.30	11.43	0.30	26.12	2.17

Note: $F_{0.95,2,2} = 19.0$

There was no significant variation in leachate quality with the three variables; therefore, the conditions to generate the acidic medium leachate for the treatability study were chosen arbitrarily but with the following reasoning in mind:

Residue Type (not significant): Bed - represents the major portion of the solid waste

L/S ratio (not significant): 20:1 - generates the largest quantity of leachate for treatability work and allows comparison with previous Dearborn/EPS leaching studies

Contact time (not significant): 24h - allows development of a parallel between the two media and allows comparison with previous Dearborn/EPS leaching studies

The results of the analysis of variance for the D.I. medium leachates (Table A5) indicated with 95% confidence that the L/S ratio did not significantly affect leachate quality. The contact time, however, did significantly affect leachate quality ($f=26.1$ is greater than $F=19.0$) as measured by sulphate, with 24 hours producing the leachate with the greatest contaminant concentration. The residue type also significantly affected leachate quality as measured by conductivity ($f=52.7$) and sulphate ($f=23.4$). Conductivity indicated that the residue that produced the leachate with the greatest contaminant concentration was the baghouse material, and the sulphate analysis indicated that it was the cyclone material. To resolve this issue, three more tests were conducted for the D.I. medium at a L/S ratio of 20:1 and a contact time of 24 hours for all three residues-bed, cyclone, and baghouse. The results presented in Table A6, show that the baghouse material produced the leachate with the greatest contaminant concentrations in terms of all the parameters tested except for sulphate.

The following conditions were chosen to generate D.I. medium leachate:

Residue type (significant): Baghouse - produced leachate with the greatest contaminant concentrations

L/S Ratio (not significant): 20:1 - generates the largest quantity of leachate for treatability work; and allows comparison with previous Dearborn/EPS leaching studies

Contact Time (significant): 24h - produced leachate with the greatest contaminant concentrations

TABLE A6 CHARACTERISTICS OF D.I. MEDIUM LEACHATE*

Parameter	Residue		
	Bed	Cyclone	Baghouse
pH	12.3	12.4	12.5
Alkalinity	2050	2150	2300
TDS	4296	4660	5422
Conductivity	9850	10 150	11 600
Calcium	1570	1620	1890
Sulphate	1630	1680	1550

Note: all values in mg/L except pH (units)
* leached at a contact time of 24 h and a L/S ratio of 20:1

APPENDIX B

CHARACTERIZATION OF AFBC LEACHATES AND TREATED EFFLUENTS

TABLE B1 CHARACTERIZATION OF UNTREATED (MASS PRODUCED) LEACHATES

Parameter	Leachate		Leaching Medium	
	Baghouse*	Bed**	D.I.	Acidic
pH	12.5	12.4	7.4	4.4
Alkalinity	2180	5000	<1	< 1
Hardness	4550	7975	<1	< 1
TDS	5312	14 318	<2	3750
Conductivity	11 200	15 000	1.35	3190
Langelier Index	+7.3	+7.9	-	-
Aluminum	< 0.01	< 0.01	<0.01	< 0.01
Arsenic	< 0.001	< 0.001	-	-
Barium	0.898	0.218	0.005	0.006
Beryllium	< 0.0005	< 0.0005	<0.0005	< 0.0005
Boron	0.105	0.038	<0.004	< 0.004
Cadmium	< 0.01	< 0.01	<0.01	< 0.01
Calcium	1820	3190	0.01	0.11
Chlorides	503	137	0.1	6.1
Chromium	0.06	< 0.01	<0.01	< 0.01
Cobalt	< 0.05	< 0.05	<0.05	< 0.05
Copper	0.017	0.014	<0.008	0.117
Fluorides	4.1	1.4	<0.15	0.10
Iron	0.09	0.09	<0.01	< 0.01
Lead	1.15	0.05	<0.05	< 0.05
Magnesium	< 0.01	< 0.01	<0.01	0.02
Manganese	< 0.01	< 0.01	<0.01	< 0.01
Molybdenum	< 0.2	< 0.2	<0.2	< 0.2
Nickel	0.07	0.09	<0.05	< 0.05
Phosphate	0.7	0.7	<0.5	< 0.5
Potassium	20	< 1	<1	7
Selenium	0.007	0.001	-	-
Silica	0.11	0.12	<0.05	< 0.05
Silver	< 0.005	< 0.005	<0.005	< 0.005
Sodium***	33	1060***	<1	1040***
Strontium	2.06	2.67	<0.001	< 0.001
Sulphate	1520	1300	<0.2	< 1
Titanium	< 0.005	< 0.005	<0.005	< 0.005
Vanadium	< 0.005	< 0.005	<0.005	< 0.005
Zinc	0.59	0.12	0.06	0.22
Zirconium	< 0.05	< 0.05	<0.05	< 0.05

Note: all values in mg/L, except pH (units) and conductivity (µS/cm) and Langelier Index (units)

* Baghouse leachate: D.I. medium, 20:1 L/S, 24 h contact time

** Bed Leachate: Acidic medium, 20:1 L/S, 24 h contact time

*** Acidic leaching medium adds significant sodium

TABLE B2 CHARACTERIZATION OF EFFLUENTS FROM TREATMENT OF BAGHOUSE MATERIAL LEACHATES*

		Treatment				
		Acid Addition		Recarbonation		
Parameter	Untreated	H_2SO_4	HCl	1-Stage	2-Stage	Aeration
pH	12.5	6.5	6.6	6.6	6.9	7.9
Alkalinity	2180	14	22	366	296	44
Hardness	4550	4075	4075	2775	2625	2305
TDS	5312	2954	5622	3874	3696	3434
Conductivity	11 200	3300	7000	4000	3900	3700
Langelier Index	+7.3	-0.8	-0.5	+0.5	+0.7	+0.9
Aluminum	< 0.01	0.38	0.10	0.69	0.72	0.88
Arsenic	< 0.001	-	-	-	-	-
Barium	0.898	0.031	0.080	0.060	0.143	0.93
Beryllium	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005
Boron	0.105	0.095	0.096	0.087	0.086	0.086
Cadmium	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Calcium	1820	1630	1630	1110	1050	922
Chlorides	503	448	1960	476	486	510
Chromium	0.06	0.04	0.03	0.02	0.05	0.06
Cobalt	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Copper	0.017	0.012	0.014	< 0.008	< 0.008	0.012
Fluorides	4.1	4.0	6.0	2.0	1.4	1.48
Iron	0.09	0.05	0.07	0.04	0.04	0.05
Lead	1.15	< 0.05	0.30	< 0.05	< 0.05	< 0.05
Magnesium	< 0.01	< 0.01	< 0.01	< 0.01	0.05	< 0.01
Manganese	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Molybdenum	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	0.3
Nickel	0.07	< 0.05	0.07	0.05	< 0.05	0.07
Phosphate	0.7	< 0.5	0.6	< 0.5	< 0.5	0.5
Potassium	20	20	18	18	19	28
Selenium	0.007	-	-	-	-	-
Silica	0.11	0.10	0.12	0.08	0.09	0.11
Silver	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Sodium	33	32	32	32	34	35
Strontium	2.06	1.47	1.93	1.39	1.56	1.84
Sulphate	1520	1300	1230	1480	1460	1530
Titanium	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Vanadium	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Zinc	0.39	0.60	0.56	< 0.05	< 0.05	0.07
Zirconium	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05

Note: all values in mg/L, except pH (units), conductivity (μS/cm), and Langelier Index (units)
* deionized water leaching medium

TABLE B3 CHARACTERIZATION OF EFFLUENTS FROM TREATMENT OF BED MATERIAL LEACHATE

Parameter	Untreated	Treatment				
		Acid Addition		Recarbonation		Recarbonation/ Aeration
		H_2SO_4	HCl	(2-Stage)	Aeration	
pH	12.4	7.3	6.9	6.8	7.9	7.7
Alkalinity	3000	2500	2250	2800	2300	2300
Hardness	7975	5025	7250	5800	5625	5475
TDS	14 318	11 422	14 272	12 554	13 080	12 102
Conductivity	15 000	8400	11 400	9000	9100	8800
Langelier Index	+7.9	+2.3	+2.0	+1.8	+2.9	+2.7
Aluminum	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Arsenic	< 0.001	-	-	-	-	-
Barium	0.218	0.172	0.210	0.094	0.112	0.087
Beryllium	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005
Boron	0.038	0.034	0.036	0.034	0.037	0.032
Cadmium	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Calcium	3190	2010	2900	2320	2250	2190
Chlorides	137	12	1500	13.3	40	15.7
Chromium	< 0.01	0.01	0.01	< 0.01	0.01	< 0.01
Cobalt	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Copper	0.014	0.010	0.013	0.014	0.009	< 0.008
Fluorides	1.4	1.4	1.45	0.95	0.95	0.95
Iron	0.09	0.06	0.08	0.08	0.06	0.06
Lead	0.05	< 0.05	0.10	< 0.05	< 0.05	< 0.05
Magnesium	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Manganese	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Molybdenum	0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
Nickel	0.09	0.07	0.08	0.07	0.07	0.07
Phosphate	0.7	0.6	0.7	0.7	0.6	0.6
Potassium	< 1	< 1	< 1	1	15	3
Selenium	0.001	-	-	-	-	-
Silica	0.12	0.10	0.12	0.14	0.16	0.15
Silver	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.05
Sodium*	1060*	1000*	991*	1060*	1120*	1060*
Strontium	2.67	2.15	2.51	2.21	2.55	2.28
Sulphate	1300	1120	1210	1410	1290	1300
Titanium	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Vanadium	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Zinc	0.12	0.13	0.13	0.08	0.08	0.08
Zirconium	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05

Note: all values in mg/L, except pH (units), conductivity (μS/cm) and Langelier Index (units)
* acidic leaching medium-adds significant sodium

TABLE B4 CHARACTERISTICS OF EFFLUENTS AFTER CALCIUM REMOVAL

Parameter	Baghouse Material Leachate			Bed Material Leachate+	
	Untreated	Soda Ash	H_2SO_4/ Soda Ash	Recarbonation	Recarbonation/ Soda Ash
pH	12.5	12.5	10.6	6.8	10.2
Alkalinity	2180	1970	2960	2300	2600
Hardness	4550	5	< 1	6400	1
TDS	5312	4900	5620	13 100	14 160
Conductivity	11 200	11 500	7520	10 000	14 000
Langelier Index	+7.3	+4.4	+2.6	+1.9	+2.0
Aluminum	< 0.01	0.04	< 0.01	< 0.01	< 0.01
Arsenic	< 0.001	-	-	-	-
Barium	0.898	0.012	< 0.005	0.105	< 0.005
Beryllium	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005
Boron	0.105	0.075	0.061	0.144	0.088
Cadmium	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Calcium	1820	2.00	0.46	2560	0.41
Chlorides	503	435	429	745	655
Chromium	0.06	0.04	0.02	< 0.01	< 0.01
Cobalt	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Copper	0.017	< 0.008	< 0.008	< 0.008	< 0.008
Fluorides	4.1	0.9	3.0	1.1	1.4
Iron	0.09	< 0.01	< 0.01	0.07	< 0.01
Lead	1.15	0.10	< 0.05	0.10	< 0.05
Magnesium	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Manganese	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Molybdenum	< 0.2	0.4	< 0.2	< 0.2	< 0.2
Nickel	0.07	< 0.05	< 0.05	0.07	< 0.05
Phosphate	0.7	< 0.5	< 0.5	0.6	< 0.5
Potassium	20	23	21	41	37
Selenium	0.007	-	-	-	-
Silica	0.11	0.19	0.06	0.10	0.38
Silver	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Sodium*	33	1760*	1880*	1020*	4520*
Strontium	2.06	0.49	0.011	3.25	0.011
Sulphate	1520	1370	2200	1230	995
Titanium	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Vanadium	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Zinc	0.39	0.10	< 0.05	< 0.05	< 0.05
Zirconium	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05

Note: all values in mg/L, except pH (units), conductivity (µS/cm) and Langelier Index (units)
+ leached at a L/S of 10:1 for 8 h (this sample only)
* soda ash and acidic leaching medium add sodium

APPENDIX C

QUALITY CONTROL DATA

TABLE C1 COMPARATIVE ANALYSIS OF A STANDARD REFERENCE MATERIAL+

Parameter	Certified Value	Measured Value	Percent Recovered
Aluminum (%)	14	14.5	104
* Arsenic	145 ± 15	139	96
Barium	1500	1330	89
Beryllium	12	12.5	104
* Cadmium	1.0 ± 0.15	<1	-
Calcium (%)	1.11 ± 0.01	1.04	94
* Chromium	196 ± 6	164	84
Cobalt	46	38	83
* Copper	118 ± 3	113	96
* Iron (%)	9.40 ± 0.10	9.25	98
* Lead	72.4 ± 0.4	60	83
* Magnesium	4550 ± 100	4560	100
Manganese	190	162	85
* Nickel	127 ± 4	115	91
* Potassium (%)	1.88 ± 0.06	2.03	108
* Selenium	10.3 ± 0.6	9.80	95
* Silica (%)	22.8 ± 0.8	22.5	99
* Sodium	1700 ± 10.0	2000	118
Strontium	830 ± 30	773	93
* Titanium (%)	0.8	0.8	100
Vanadium	300	310	103
* Zinc	220 ± 10	232	105

Note: + National Bureau of Standards Fly Ash 1633a
* certified values, all other parameters are included for additional information only
all values in mg/kg except otherwise specified

TABLE C2 REPLICATE ANALYSES OF BAGHOUSE MATERIAL LEACHATE

Parameter	Initial Observed Values (November 22, 1984)	Later Observed Values (January 17, 1985)
pH	12.5	12.5
Alkalinity	1980	2180
Hardness	4630	4550
TDS	5200	5300
Conductivity	11 100	11 200
Aluminum	< 0.1	< 0.1
Arsenic	-	< 0.001
Barium	0.910	0.898
Beryllium	< 0.0005	< 0.0005
Boron	0.100	0.105
Cadmium	< 0.01	< 0.01
Calcium	1850	1820
Chlorides	513	503
Chromium	0.06	0.06
Cobalt	< 0.05	< 0.05
Copper	0.014	0.017
Fluorides	6.5	4.1
Iron	0.08	0.09
Lead	1.00	1.15
Magnesium	< 0.01	< 0.01
Manganese	< 0.01	< 0.01
Molybdenum	< 0.2	< 0.2
Nickel	0.06	0.07
Phosphate	0.6	0.7
Potassium	18	20
Selenium	-	0.007
Silica	0.09	0.11
Silver	< 0.005	< 0.005
Sodium	33	33
Strontium	2.07	2.06
Sulphate	1470	1520
Titanium	< 0.005	< 0.005
Vanadium	< 0.005	< 0.005
Zinc	0.51	0.59
Zirconium	< 0.05	< 0.05

Note: all values in mg/kg except pH (units) and conductivity (µS/cm)